THE MANUFACTURE OF VARNISHES

AND

KINDRED INDUSTRIES

VOLUME III.

SPIRIT VARNISHES AND SPIRIT VARNISH MATERIALS

THE MANUFACTURE OF

VARNISHES

AND

KINDRED INDUSTRIES

BASED ON AND INCLUDING THE "DRYING OILS AND VARNISHES"
OF

ACH. LIVACHE

BY

JOHN GEDDES McINTOSH

LATE LECTURER ON VARNISH MANUFACTURE AT THE POLYTECHNIC, REGENT STREET, AND
THE BOROUGH POLYTECHNIC

SECOND, GREATLY ENLARGED, EDITION, IN THREE VOLUMES

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SPIRIT VARNISHES AND SPIRIT VARNISH MATERIALS

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PREFACE TO SECOND EDITION, VOL. III.

THE manufacture of spirit varnishes is quite a distinct industry altogether from that of oil varnishes. The question then arises wherein do the two classes of varnish differ, and when should we use a spirit varnish in preference to an oil varnish and *vice versa*.

Fewer hands are employed in making spirit varnishes than in oil varnish manufacture, for the reason that in making spirit varnishes all you have to do is to take your alcohol and shellac and put them in a churn, set the machinery going, and it "cuts" itself. Whereas, in making oil varnishes, you have to have fire-places and kettles; you must have a man stand over each kettle and look after the melting of the material. It has to be put into tanks to settle, which does not have to be done in the case of shellac varnishes. In oil varnish-making you must have a plant with chimneys and everything constructed for it. On the other hand, you can make spirit varnishes in any little shanty where-ever you may be. It would not require any invested capital except in the merchandise alone. Take the orange shellac that they import: all you have to do is to put that with alcohol and agitate it. There is nothing else to do. One man could run twenty churns so far as looking after them is concerned. He would turn out a lot of stuff. In America, however, all finely-finished pieces of furniture as a rule are finished with what we in Great Britain call oil varnishes, and then they are polished and rubbed, but as a rule that is applied over one or two coats of shellac. Shellac varnish has to be used to preserve the colour of the finished product of the rattan chair industry. A varnish "cut" with oil will turn yellow. All oil varnishes do so, but a shellac varnish "cut" with alcohol, whether grain or wood alcohol, does not become yellow. On work that requires a high polish, a distinctively durable finish to last a long time, where the element of time in finishing the goods is not considered, an oil varnish would be better than an alcohol varnish. There are some goods where an oil varnish is distinctively better than an alcohol varnish, but there are very many other goods on which an alcohol varnish would be used.

In the rattan chair business alcohol varnish or shellac is about the only finish that can be used to keep the goods white.

It is almost an essential. In fact, until the advent of collodion and celluloid spirit varnishes, it had never been possible to find a substitute for shellac varnish "cut" either with grain alcohol or with wood alcohol that would preserve the white colour of the goods which is necessary to maintain their beauty.

In the general chair business, it expedites the finish to use shellac in some form instead of using an oil varnish, which takes from one to three days to dry, while a shellac varnish will dry in a few hours. That is to say, goods can be produced from their raw state, that is, from the state in the white, ready to be dispatched in one day if necessary by using shellac varnish, while by using regular oil varnish it takes three days at least, ordinarily more. Time in a factory means money, because the men get a good many more articles finished in the same period of time. The same amount of labour turns out a much larger product, and the same amount of space room will turn out two to three times the product on many kinds of goods.

Coming to other industries, a carriage does not take up varnish like a house does. A large building takes a great deal of varnish. It is furniture that consumes varnish, especially spirit varnish. With oil varnish, on the other hand, a carriage man will give an order for a barrel where a builder in a large way will take several. The present high price of all raw materials is bringing about quite an anomalous state of affairs. The difference in cost between a high and a low-priced varnish comes in thus, says an American varnish-maker: we can use benzine at 8½ cents a gallon for the solvent, and we can use Manila gum at 10 cents a lb., whereas we pay a dollar a lb. for goose flesh, and then have to prepare the oils in the most expensive manner possible. Signs are not awanting that strenuous efforts are being made by interested parties posing as public benefactors to "educate" the trade to the use of low-grade raw materials which can in no way be regarded as substitutes for the products they are intended to replace. They are not even make-shifts, and those who listen to the voice of the charmer will most assuredly reap the harvest they have sown. A good trade name is after all better than a golden girdle.

J. G. M.

LONDON, *May*, 1911.

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PART I.

SOLVENTS.

CHAPTER I.

CHARACTERISTICS OF SPIRIT VARNISH SOLVENTS OR DILUENTS.

If the solvents more or less available for use in the spirit varnish trade are somewhat numerous, yet only a comparatively small number of these are to any great extent actually used, for the very sound reason that, if many be dear, few are efficient. The scarcity of spirits of turpentine has brought a very excellent solvent indeed, petroleum spirit, to the fore; it, in many cases, is just as valuable a solvent as spirits of turpentine, and that even if it were sold at the same price as the latter. For many purposes it is indeed superior to spirits of turpentine, for instance, as a solvent for rosin, it leaves a more hard and far less tacky coat than spirits of turpentine does. The chief points to be observed in selecting solvents are the following:—

1. Freedom from acidity, turbidity, and all impurities.
2. Solubility in and affinity for water, and the percentage of water present if the solvent be soluble in water.
3. Colour, if any and if readily decolorized.
4. Smell, if any and if readily deodorized.
5. Flash-point if possible above 73° F.
6. Miscibility with other solvents.
7. Price.
8. Constancy of supply, more especially in time of war.
9. Solvent capacity.
10. Rapidity of evaporation, and freedom from residue.
11. Density or specific gravity.
12. Viscosity and conversely limpidity.

1. *Freedom from Acidity.*—The free acid, and other noxious impurities, in methylated spirit are a source of trouble, causing blooming, chilling, etc., of the varnish film in cold, damp, raw weather. The acidity of spirits of turpentine, if due to acetic acid or similar acids, is highly objectionable and a fruitful cause of corrosion; when used to dilute or thin inert pigments (in paints) which cannot kill this acidity, such acid spirits of turpentine must do incalculable mischief by starting metallic corrosion at the very outset. Neither methylated spirit nor spirits of turpentine should turn blue litmus red. If solvents react acid, the acidity should be corrected prior to use, in the case of spirits of turpentine, by filtration through quicklime followed, if need be, by rectification. As to methylated spirit reacting acid, nothing can be done without excise permission. The

varnish-maker would do well to buy only from neutral samples of all solvents and insist on deliveries being absolutely neutral.

2. *Solubility in and Affinity for Water.*—This is far from an advantage. If we take the case of a substance only volatile at a somewhat high temperature, e.g. sulphuric acid, which has an affinity for water, and pour some of it into a saucer in a cold, raw, damp atmosphere so as to fill the saucer about one-half and leave it for say a couple of days, the contents of the saucer will then be running over. Now, alcohol has as great an affinity for water as sulphuric acid has, but the strong alcohol in a spirit varnish film, as applied, is volatile, and passes away into the air before it can absorb much water. But the alcohol in the varnish, if already somewhat weak, may absorb quite enough water from the damp, cold, raw air (which keeps the alcohol longer in contact with the water than warm air does) to thoroughly chill the varnish, causing it to bloom and exhibit all the numerous bad effects which a varnish applied under such conditions must perforce exhibit. To sum up, the alcohol if weak is not too weak to prevent it becoming still more dilute by attracting a further quantity of moisture from the air, and this contingent from the air goes to swell the amount of water originally present in the alcohol, and the aggregate of the two amounts of water are concentrated in the last dregs of the solvent left in the varnish film.

3. *Colour.*—All solvents should be water-white and kept in well-tinned vessels. Black camphor oil, for instance, has some merits as a solvent, but it should be rectified and so decolorized prior to use, and so on with other dark solvents. But it is useless to expect a free acid solvent to remain colourless unless stored in glass or porcelain: it must perforce attack the metals or solder and become coloured.

4. *Smell.*—The idiosyncracies of workmen must be considered. The olfactory nerves of some are more sensitive than others. Many persons object to the smell of such solvents as turps, amyl acetate, amyl alcohol. The smell of unrectified carbon disulphide is abominable. But dehydrated green vitriol deodorizes it, and many other evil-smelling solvents, such as unrectified petroleum spirit. But some tolerate the smell that others abhor.

5. *Flash-point.*—A low flash-point brings the solvent under the Petroleum Acts, and that restricts sale, but sufficient attenuation of certain varnishes and the requisite rapidity of evaporation to a non-tacky coat can only be secured by the use of low-flash products.

6. *Miscibility with other Solvents.*—Here we have one of the great defects of alcohol—it will not mix with fixed oils, castor-oil and croton-oil excepted, nor with petroleum products. Deficiency as regards miscibility with oils is characteristic of all solvents which dissolve in water in all proportions. A solvent that dissolves in water, however great its solvent power for the solid which it is used to dissolve, is a defective solvent from a varnish point of view, because it leaves water even at a high temperature; witness the "bumping" of an ethereal solution of fatty acids; as it gets near to dryness the

water is ejected as steam in spurts, throwing the fatty acids in every direction. Here we have another proof that in the evaporation of a spirit varnish, in which aqueous spirit is used, the water is concentrated in the varnish film until the last stage of drying, when it makes itself felt in blooming and countless other defects. The principle to bear in mind is that like solvents are mutually intermiscible. All coal-tar products used as solvents dissolve each other; benzene dissolves xylene. The same principle applies to petroleum products. Gasolene is an excellent thinner for the more heavy white spirit. Pure methyl alcohol, a wood-tar distillation product, if our excise allowed it to be used, would be a highly useful spirit varnish solvent from both the evaporative point of view and solvent capacity. It would decidedly increase the volatility of spirit varnishes. Again acetone is another wood-tar product, and it also mixes with methyl alcohol in all proportions.

7. *Price.*—The intelligent varnish-maker knows very well that he cannot use a solvent selling at double or treble the price per gallon that he can get for it as a constituent of varnish.

8. *Constancy of Supply at a Fair Price.*—Acetone is no doubt an excellent solvent in many ways, but there is every reason to believe, as it takes a "forest" of timber to produce a ton of acetone, that it will get higher in price as timber every day grows scarcer. Needless to say, it would rise to famine prices in case of a great war. Varnish-makers who relied on acetone as a solvent would then find themselves in a serious predicament.

9. *Solvent Capacity.*—Each solvent has its special use and is used to dissolve some particular line of resins. Alcohol is the best solvent for shellac and sandarac, spirits of turpentine for mastic, dammar, and common rosin. Amyl acetate, acetone, ether, acetic ether, or a mixture of these, form suitable solvents for celluloid. Carbon disulphide is the solvent *par excellence* for india-rubber and gutta-percha. It has been known for over a century that camphor and its congeners aid solution of copal in turps or methylated spirits, hence the virtue of terpineol as a copal solvent or of essential oils containing congeners of camphor, e.g. cajeput oil, rosemary oil. Too great results are expected from terpineol as a solvent for "copal".

Too implicit reliance should not be placed in tables of solubility. Some of them show at a glance that the operator was not a master of his subject. As regards other tables, if the skill of the operator cannot be called in question, the fact remains that the analysis is only made either on a single lump or a single delivery. The amount left insoluble by any partial solvent for a resin will not only vary with each batch of resin, but with each lump of each resin, which has perforce a distinct history of its own. It may safely be said that no two operators working independently with the same solvents and pieces from the same lump of the same resins will get identical or even comparable results in the case of intractable resins. The solution of an intractable resin is like the get-

ting of a startled animal through a gate. One man can easily coax it through, another either runs for his life or still further frightens the animal so that it bolts away on another path. So it is with resins. Solution is often effected readily by the turn of the wrist, by the skill and by the tact of the practical man. The operator who tries to force solution, if he does not get severely burnt for his pains, generally gets a slimy agglutination as his reward. The varnish-maker, in trying to find the best solvent for a new resin, should consult Coffignier's or other reliable tables. Suppose he wants the most powerful solvent for ceresin, then he would consult the following table, which shows carbon disulphide to rank first, petroleum ether running it a close second :—

TABLE I.—SOLUBILITY OF CERESIN IN VARIOUS SOLVENTS.

Solvent.	Density.	Boiling-point °C.	Ceresin in grammes dissolved by :—		Solvent in grammes to dissolve 1 part Ceresin.
			100 grms.	100 c.c.	
Carbon disulphide	—	—	12·99	—	7·6
Petroleum ether	0·7233	up to 75	11·73	8·48	8·5
Turps	—	158-166	6·06	5·21	16·1
Cumene com.	0·867	up to 160	4·28	3·72	23·4
Cumene	0·847	150-160	3·99	3·39	25·0
Xylene com.	0·866	135-143	3·95	3·43	25·1
Xylene	0·864	136-148	4·39	3·77	22·7
Toluene	0·866	108-110	3·83	3·34	26·1
Toluene	0·866	108·5-109·5	3·92	3·41	25·5
Chloroform	—	—	2·42	3·61	41·3
Benzene	—	—	1·99	1·75	50·3
Ethyl ether	—	—	1·95	—	50·8
Isobutyl alcohol	0·804	—	0·285	0·228	352·9
Acetone	0·797	—	0·262	0·209	378·7
Ethyl acetate	—	—	0·238	—	419·0
Ethyl alcohol	—	—	0·219	—	453·6
Amyl alcohol	0·813	127-129	0·202	0·164	495·3
Propionic acid	—	—	0·165	—	595·3
Propyl alcohol	—	—	0·141	—	709·4
Methyl alcohol	0·798	65·5-66·5	0·071	0·056	1447·5
Methyl formate	—	—	0·060	—	1648·7
Acetic acid	—	—	0·060	0·063	1668·6
Ethyl alcohol	—	—	0·046	—	2149·5
Acetic anhydride	—	—	0·025	—	3856·2
Formic acid crystals	—	—	0·013	0·015	7689·2
Ethyl alcohol	—	—	0·0003	—	33000·0

When a varnish-maker receives a new resin for trial, he should either go to work himself or set his chemist to work to determine and tabulate its solubility.

10. *Rapidity of Evaporation.*—Here it is impracticable to use such a solvent as spirits of turpentine if the varnish has to dry in ten to fifteen minutes. Such a result can only be got by the use of petroleum spirit, say 75 per cent by vol. of petroleum spirit and 25 per cent by vol. of gasolene. The gasolene as it evaporates whirls the petroleum spirit along with it.

11. *Density.*—Great density in the solvent is not always required. When a heavy solvent is used in enamels it may, however, prevent to some extent the separation of the vehicle from the pigment. But when the density of the solvent is doubled, so also is the railway account for the carriage of varnishes in which such heavy solvents figure. Moreover the density is so far an index of purity that the hydrometer should be in constant use in buying solvents.

12. *Viscosity.*—Too mobile a solvent is not always an advantage, neither is a too viscous one. Spirits of turpentine is somewhat too viscous for certain purposes, whilst ether and gasolene are too mobile. The practical man knows the happy medium which does not lend itself very well to verbal expression.

So as to explain the plan of this, Part I of this Volume, and thus facilitate reference; it may be well to state that the solvents to be described in the sequel are taken in alphabetical order as far as due regard to logical sequence will allow:—

CHAPTER II.

SOURCE, PREPARATION AND USES OF VARIOUS SOLVENTS.

1. *Acetic Acid.*—Chemical formula, $C_2H_4O_2$; molecular weight = 60; melting-point, 16·5° C.; boiling-point, 118° C.; specific gravity, 1·080 at 0° C.: at 20° C. density, $\frac{t}{4}$ = 1·0495; index of refraction, 1·36985, H″; molecular refraction, $p\frac{n-1}{d}$; determined, 21·15; calculated, 21·4; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; determined, 12·93; calculated, 13·04.

It is an excellent solvent for many organic compounds, particularly resins. But owing (1) to the suffocating odour of the strong acid, its highly corrosive action on many metals and on the skin, (2) to its hygroscopic nature, (3) its high boiling-point and consequent slow evaporation, it is impracticable to use it in the free state as a solvent for resins in varnish-making. In the combined state as ethyl and amyl acetate, it finds a use as a solvent for celluloid, and in combination with cellulose itself, as cellulose acetate, it forms a substitute for celluloid less brittle than celluloid itself.

2. *Acetic Anhydride.*—Chemical formula, $(CH_3CO)_2O$; molecular weight, 102·1; fluid, boiling-point, 138° C.; density at 20° C., $\frac{t}{4° C.}$ = 1·0815; index of refraction (at above temperature), 1·36985; molecular refraction, $p\frac{n-1}{d}$; determined, 36·63; calculated, 37·4; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; determined, 12·93; calculated, 13·04.

Acetic anhydride is a mobile liquid with an unpleasant, irritating odour. Alkalies water, and all substances, except acids which contain the hydroxyl group, decompose acetic anhydride, acetyl derivatives being formed. Its main use is in oil and resin analysis.

3. *Acetone.*—Chemical formula, C_3H_6O, molecular weight = 58; $D\frac{t}{4}$ at 20° C. = 0·7920; molecular refraction, $p\frac{n-1}{d}$ = 26·16; calculated, 26·2; molecular refraction, $\frac{P\,n^2-1}{(n^2+2)d}$ = 16·05; calculated =

16·02. Pure acetone is obtained by rectifying the crude distillate from the dry distillation of acetate of lime. It is a colourless liquid having a peculiar ethereal odour and a burning taste, a specific gravity of 0·814, and a boiling-point of 55·3 at 0 C. It is miscible with ether, alcohol, and water in all proportions. Commercial acetone should not have a specific gravity greater than 0·802 at 15° C., and four-fifths of it should distil below 58·8° C. It is an excellent solvent for resins, gums, camphor, fats, and gun-cotton, and is largely used in the manufacture of smokel ss powder, the preparation of celluloid goods, chloroform, iodoform, and sulphonal. Acetone is also manufactured from crude wood spirit, of which it is an important constituent, by the continuous rectification plant designed by E. Barbet of Paris, now in use both in France, Canada, and the United States of America. The crude wood spirit contains about 25 per cent of acetone, and the plant yields acetone of 95 to 98 per cent purity.

Testing of Acetone.—(1) It should be limpid and pale. (2) It should mix with water in all proportions. (3) The acetone should be neutral and mark 98·5 at 15 C. (59 F.) by the alcoholmeter. (4) On distillation, 95 per cent of the liquid should distil at 58° C. (136·4° F.). (5) A solution of mercuric chloride should give no turbidity with acetone. (6) The acetone should not contain more than 0·1 per cent of aldehyde, which is determined by reduction by a solution prepared from 30 grammes of nitrate of silver, 30 grammes of caustic soda and 200 grammes of ammonia (of 0·900 density), all dissolved in distilled water to 1 litre; 10 c.c. of acetone are taken, its volume of distilled water and 2 c.c. of the silver solution added; it is left for a quarter of an hour in darkness, then it is tested by ammonium sulphide to see if there be nitrate of silver in excess; if not, the acetone contains more than 1 per cent of aldehyde. (7) By Messinger's iodometric assay 98 per cent at least should be obtained.

4. *Amyl Acetate.*—Chemical formula, $CH_3CO_2C_5H_{11}$; molecular weight, 130·1; density, 0·857 fluid, boiling-point, 148 C.; index of refraction at 20° C. (D 0·8561), 1·40168; molecular refraction, $p\frac{n-1}{d}$; found, 13·94; calculated, 13·8; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; found, 8·52; calculated, 8·48. The preparation of this ether is carried out in the same way as that of ethyl acetate from acetate of soda, sulphuric acid, and amyl alcohol. The rectified product is washed with water, then set aside to dry over calcium chloride and rectified with a little lead ox de. Berthelot advises that the crude product be washed with acetic acid, diluted with its own weight of water, so as to remove traces of amyl alcohol which separate with difficulty; it is then washed with water, dried over chloride of calcium and finally rectified over lead oxide. Amyl acetate is a colourless liquid, boiling at 125° C.; its density is 0·876 at 0° C.; it is insoluble in water, but soluble in alcohol and

ether. Its aromatic ethereal odour, recalling the pear, has induced confectioners to use it in certain saccharine preparations. It likewise enters into the composition of some perfumes, so as to impart to them a more pleasant odour, as well as into certain extra fine petroleum products (*pétroles de luxe*), but it is chiefly used as a solvent of pyroxylin or nitrocellulose in the manufacture of spirit varnishes of the Zapon type.

5. *Amyl Alcohol* (Isoamylic alcohol fermentation amyl alcohol, $(CH_3)^2CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$).—Chemical formula (Empirical), $C_5H_{12}O$; molecular weight, 88; density, 0·825 at 0° C.; boiling-point, 129° C.; flash-point, 42° C.; index of refraction (t = 20° C.; D 0·8123) = 1·40573; molecular refraction, $p\frac{n-1}{d}$; found, 43·99; calculated, 43; molecular refraction, $p\frac{n^2-1}{(n_2+2)d}$; found, 8·52; calculated, 8·48. Ordinary or fermentation alcohol is one of the eight possible alcohols of the formula $C_5H_{12}O$. The physical constants of five of these are given in the following table:—

TABLE II.—CHEMICAL AND PHYSICAL CONSTANTS OF ISOMERIC AMYL ALCOHOLS.

Isomers	Formula.	Molecular Weight.	Density.	Melting-point.	Boiling-point °C.
Amyl alcohol, Diethylcarbinol	$(C^2H^5)^2{\cdot}CH{\cdot}OH$	88	0·8315/0° C.	—	116·3
„ norm.	$C^4H^9{\cdot}CH^2{\cdot}OH$	„	0·8296/0° C.	fl.	137
„ Fermentation, Iso-	$(CH^3)^2CH{\cdot}CH^2{\cdot}CH^2{\cdot}OH$	„	0·825/0° C.	fl.	129
„ second., Methylpropylcarbinol	$C^2H^5{\cdot}CH^2{\cdot}CH(OH){\cdot}CH^3$	„	0·825/0° C.	fl.	118·5
„ second., Methylisopropylcarbinol	$(CH^3)^2{\cdot}CH{\cdot}CH(OH){\cdot}CH^3$	„	0·829/0° C.	fl.	112·5

Scheele was acquainted with amyl alcohol in its impure state as fusel oil. Dumas determined its composition in 1834. Cahours in 1837 pointed out its analogy with ordinary alcohol, an analogy which was confirmed by the researches of Dumas and Stas, but more especially by those of Balard.

The fusel oil, which is the last body to come over in the distillation of alcohol (whether from malt, wine, potatoes, or beetroot), consists principally of amylic alcohol.

Amyl alcohol is invariably present in fermentation alcohol, but its formation therein is obscure. Commercial fusel oils of different degrees of purity are to be found on the market. Commercial fusel oil contains only about 80 per cent of pure amyl alcohol. To obtain it pure the fusel oil is washed with water, and the portion

which passes over between 128° and 132° C. is collected apart. The portion distilling over below 128 contains butylic alcohol. Five c.c. of pure amyl alcohol mixed with concentrated sulphuric acid should only give a faint yellow or reddish colour. The commercial amylic alcohol is coloured black to brownish by sulphuric acid. Amyl alcohol, colourless when mixed with sulphuric acid, can only be obtained by repeated tedious treatment with concentrated sulphuric acid, and quite pure amyl alcohol can only be got by decomposing pure amyl sulphate. Amyl alcohol is a clear colourless liquid without action on litmus paper, but on keeping a bottle on the laboratory shelves, however clear and colourless it be at first, it turns brownish by age, a fact which militates against its use in those spirit varnishes where a pale water-white colour is essential; besides amyl alcohol possesses a most disagreeable odour, and the vapour is most irritating to the throat and lungs, causing persistent coughing, and thus preventing its use as a solvent to the extent its superior solvent capacities for resins entitle it. Anyone who has the slightest regard for the comfort of those who make or use spirit varnishes, or come in contact with or even in proximity to articles on which they are applied, should consider well before they use amyl alcohol as a solvent. In straw-hat polishes it is especially objectionable, as one such straw hat in a warm room will suffice to set the whole audience coughing months after the application of the amyl alcohol stain to the hat. This seems to point out that the amyl alcohol is retained by the layer of dried stain. With a pale water-white varnish the film would be liable to be darkened on age by this retention of the amyl alcohol. Rabatte uses amyl alcohol as a potash solvent (1) in oil analysis and (2) technically to neutralize free acid in rosin oil. It has a burning taste and is the maddening principle in new raw grain whisky. It dissolves in alcohol and ether, carbon disulphide, essential and fatty oils, but is only sparingly soluble in water (1 in 39 at 16·5° C. will stand 1 in 50 at 13-14, and the solution becomes milky at 30° C.). It dissolves in all proportions in dilute acetic acid (1 : 1). It deviates the plane of polarization to the left, but to a different extent according to its source. Amyl alcohol does not take fire by contact with a flame, and when dropped on paper does not leave a permanent greasy stain. Ten grains evaporated on the water bath should leave no residue.

Ordinary amyl alcohol is a mixture in varying proportions of two isomerides, one of which is inactive and the other levo-rotatory. By converting the mixture into amyl sulphuric acid and neutralization with barium carbonate, the two isomeric alcohols can be separated, as the barium salt of the active alcohol is two and a half times more soluble in water than that of the inactive alcohol.

CHAPTER III.

SOLVENTS—(*CONTINUED*).

6. *Benzene, its derivatives and its homologues, Toluene, Xylene, Solvent Naphtha.*—Ordinary crude coal-tar naphtha (this treatise, Vol. II, pp. 34-7) is a dark-brown liquor with an unpleasant smell and a characteristic fluorescence or bloom. Its density varies from 0·840 to 0·940 and upwards. Scottish crude naphthas vary in density from 0·868 to 0·876. London naphthas range higher, viz. from 0·883 to 0·888. On distillation it evolves much ammonia. Like most products of destructive distillation its composition is highly complicated. Crude naphtha contains the most volatile principles of coal-tar, but is always accompanied by difficultly volatile products. It not only contains benzene and its homologues, but appreciable amounts of phenol, naphthalene and other volatile bases, pyrogenated resins, etc. Amongst the readily volatile substances are methane, marsh gas, olefins, carbon disulphide, mercaptans, nitriles.

Fractional Distillation Tests of Crude Naphtha.—The crude naphtha is distilled in a retort, collecting distillate in two fractions; that distilling below 160° C. gives the percentage of *once-run* naphtha, that between 160° and 180° C. the proportion of medium naphtha. Each of these distillates may be still further rectified in a bulb-tube apparatus (taking sufficient once-run naphtha to yield 100 c.c. distillate below 100° C. to confirm it as 90 per cent benzol), and that fraction of the once-run naphtha which then distils below 100° C. gives the percentage of 90 per cent benzol; that from 100° to 120° C. beginning to distil at 108° to 110° C. and yielding 88 to 90 per cent of distillate at 120° C. gives the percentage of toluene, the fraction distilling from 120° to 160° C. the percentage of solvent naphtha. The results got by the bulb-tube apparatus agree closely with those got in the works.

TABLE III.—FRACTIONATION OF CRUDE NAPHTHA.

Laboratory.	Percent	Works.	Per cent.
Below 100° C.	30	90 per cent benzol	31-32
Between 100°-120° C.	15	Toluene	14-16
" 120°-160° C.	20	Solvent naphtha	12-15

Once-run Naphtha.—Crude naphtha is generally re-distilled as it is to obtain once-run naphtha. An intermediate fraction medium naphtha is sometimes produced. It consists of the fraction from the crude, which on re-distillation passes over between 160° and 180° C. But benzene can even be separated from this latter fraction by a column still. Once-run naphtha is a fluid oil of density 0·886 to 0·892. Before rectification it is treated by concentrated sulphuric acid and alkalis. The rôle of the sulphuric acid is a multifarious one. It combines with the bases, aniline, etc.; it destroys the pyrogenated resins; it dissolves the olefins, and in general it eliminates all the bodies on which it acts. Moreover, it forms, with the naphthalene and the phenol, sulpho-conjugated acids which dissolve in the excess of acid. The use of alkalis (caustic soda) is of less importance than in the refining of petroleum, shale oil, lignite oil, or heavy coal-tar oil, because in the former there are very few phenols, the elimination of which is the principal object of this operation. That is why the treatment of once-run naphtha is, generally, started with sulphuric acid, followed by a light soda treatment to eliminate either the remainder of the phenols or the sulphuric acid and sulpho-conjugated acids remaining in solution. The amount of acid used depends on the naphtha—1 lb. per gallon (Lunge). The acid used in refining has an average density of 1·365, equal to 45 per cent. It forms a troublesome waste product. After running off the acid the naphtha is washed with water and then by 20° Tw. soda lye. The amount cannot be determined beforehand, it varies with the naphtha. The loss in refining averages 8 gallons per 100 gallons of once-run naphtha. With good naphtha it frequently falls to 5 and even 4 per cent, but bad products may lose 12 per cent. Not only do recently distilled naphthas require less chemicals in refining than old naphthas, but the loss in refining is less. The refining complete, the once-run naphtha, the washed product, is steam-distilled, and the final products, benzene, solvent naphtha, etc., collected. A still exactly like the crude naphtha still is employed. The condenser coil may be all of lead, and, on account of the volatility of benzene, should be of sufficient length. The fractionation is solely conducted by the indications of the thermometer. The fixed points of the fractionation vary with the nature of the final product desired. In making 90 per cent benzene the first fraction must be collected at 110° C., the second at 140° C., the third at 170° C., and then stop. The first fraction, again distilled by steam, then yields much 90 per cent benzol. But if it be desired to make 50 per cent benzol two fractions suffice, the first up to 140° C., the second from 140° to 170° C. The distillation of 770 gallons takes eight to nine hours, so that a distillation can easily be finished in a day. The still seldom requires cleaning. Lunge gives the following data:—

TABLE IV.—FRACTIONATION OF 50 PER CENT BENZENE FROM NAPHTHA (LUNGE).

Crude Material.	Distillate up to 140° C. first product. Volume, per cent.	Distillate from 140° C. to 170° C. second product. Volume, per cent.	Residue. Volume, per cent.
Naphtha purified spirit	60-61	15-17	20-22
„ from light oil	30-33	40	—
Mixture of the two	48-52	22-26	—

The last stage in the rectification of light oil is always effected by steam, either by indirect heating or by direct injection into the liquid. The stills are always fitted with a partial condensation apparatus or a dephlegmator, so as to separate the products as completely as possible. The steam should have a pressure of at least 2½ atmospheres—a greater pressure is advisable. Moreover, in place of condensers or dephlegmators, several distillers use large capitals or rectifying columns like Egrot's. By means of apparatus working on the principle so long applied to the rectification of alcohol, a far more perfect separation of the hydrocarbides is possible than by the older methods. As already pointed out, Mansfield, so far back as 1847, was the first to propose the use of apparatus based on the principle of dephlegmation, but it was Coupier who was the first to introduce—in an imperfect form, it is true—this idea into actual practice, and thus to prepare on a large scale the different hydrocarbides in an almost pure state. Coupier showed, in the following graph, the amount of the chief products obtained by

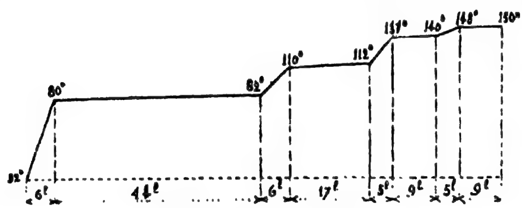


FIG. 1A.—Coupier's Graph.

distilling 100 litres of benzol beginning to boil at 62° C. and rising up to 150° C., that is to say, a 50 per cent benzol, according to the usual commercial term. The intermediate products in the sloped parts of the line of temperature are again fractionated separately. Thus, besides the forty-four parts of pure benzene and seventeen parts of pure toluene, there are obtained (*a*) six parts of light spirits, composed in part of carbon disulphide, olefins, etc., which cannot be used, and which are generally added to the solvent naphtha; (*b*) 6 per cent of a product intermediate between benzene and toluene, which is again rectified; (*c*) about 27 per cent of the higher boiling-points, which formerly were not separated but mixed with the solvent naphtha, but which are now fractionally distilled so as to prepare commercially pure xylene.

TABLE V.—FRACTIONAL DISTILLATION OF YORKSHIRE AND WIGAN CRUDE NAPHTHAS.

°C.	A.	A′.	B.	B′.	C.	C′.
	%	%	%	%	%	%
95	—	15	—	14	—	15
100	16	39	—	38	—	40
110	—	75	17	73	18	74
120	34	80	38	89	120	90
130	47	—	49	—	47	—
140	—	—	58	—	57	—
150	—	—	69	—	68	—

A = The test yields per cent of 500 gallons Yorkshire crude naphtha.
A′ = The dephlegmator yields of first 250 gallons from A.
BC = The test yields per cent of two lots of 500 gallons of Wigan crude naphtna.
B′ C′ = The dephlegmator yields per cent of first 200 and 260 gallons respectively from B and C.

Solvent Naphtha.—It will be seen that a fair average English crude naphtha, yielding about 35 per cent at 120° C., will give 50 per cent or thereabouts of commercial 40 per cent benzene. The second portion collected from the distillation which contains non-nitrifiable hydrocarbides mixed with some toluene, xylene, cumene was generally sold as solvent naphtha, or was again subjected to fractional distillation, in order to recover some toluene and crude xylene. Solvent naphtha derives its name from its extensive use as a rubber solvent in the waterproofing industry. It is also used in the purification of crude anthracene, and is one of the best solvents for metallic rosinates, such as copper rosinate. It yields some 8 to 30 per cent of distillate below 130° C., and 90 per cent below 160° C. The density of solvent naphtha should not be greater than 0·875. In composition it is complex and variable, but it consists essentially of isomeric xylenes and cumenes and a few per cents of naphthalene, an objectionable ingredient. At one time solvent naphtha included the whole fraction from the rectification of once-run naphtha, which distilled over after the benzols and below 160° C., but when xylene by itself became an article of commerce the bulk of it was separated, and thus the solvent capacity of the solvent naphtha was deteriorated.

The term 90 *per cent benzol* [D. (English) = 0·880 – 0·888, (Scottish) = 0·870 or under] is applied to a product of which 90 per cent by volume distils under 100° C. Good samples do not commence to distil below 80° C., and the percentage of distillate at 85° C. should not exceed 20 to 30 per cent, or greatly exceed 90 per cent at 100° C., and distillation should be complete under 120° C. An abnormally large distillate, say 35 to 40 per cent at 85° C., points to the presence of carbon disulphide or light hydrocarbides in undesirable proportions. The percentage proximate composition

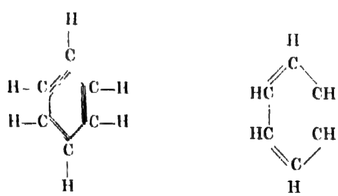
of a good 90 per cent benzol may be taken as 70 per cent of benzene, 24 per cent of toluene, and 4 to 6 per cent of carbon disulphide and light hydrocarbides. The actual amount of real benzene present may decrease to 60 or increase to as much as 75 per cent. (Allen).

The term 30 *per cent benzol* (D = 0·875) is applied to a product 30 per cent of which distils below 100° C. and 60 per cent additional between 100° C. and 120° C. Its chief constituents are toluene (pp. 16-18), and xylene (p. 19).

The term 50 *per cent* (50/90) *benzol* (D. English = 0·878 – 0·880, Scottish, 0·867 – 0·872) is applied to a product 50 per cent by volume of which distils over below 100° C. and 40 per cent additional under 120° C. (making 90 per cent in all below 120° C.) and completely distilling under 130° C. This product contains little or no CS_2. The proportion of light hydrocarbons is small, but the toluene and xylene content is naturally much greater than in 90 per cent benzol.

6*a*. *Benzene* [Chemically pure].—Chemical formula (Empirical), C_6H_6.

Kekule's constitutional formula: the benzene ring enables us to show how benzene can be regarded as formed from 3 molecules of acetylene $3(CH \equiv CH) = C6H6$. Group the 3 molecules of acetylene so that the 6 atoms of carbon occupy the apices of a regular hexagon. Suppose one of the three links joining the two groups CH disappears and is replaced by a link between the two adjacent molecules of acetylene, and then we have what is called the benzene ring, thus: —



Three molecules of acetylene = one molecule of benzene.

Molecular weight = 78·1. Density at 0° C. = 0·8991 Kopp; 0·8957 Warren; at 15° C. = 0·882 Warren; 0·87907 at 20° C. From benzoic acid at 0° C. = 0·9002; at 15° C. = 0·8846; at 30° C. = 0·8689; at 80° C. = 0·8133 Adrienz. From coal-tar = 0·9102 at 0° C. Adrienz; 0·8850 at 15° C. Nichol. Index of refraction (density d^t_4 temp. 28° C.) = 1·49157. M.Pt., 5·5° C. B.Pt., 80·5° C.

Benzene was discovered in 1825 by Faraday ("Philosophical Transactions," 1825, p. 440). It is quite an illusion to describe benzol as having been first discovered in its present grand source, viz. coal-tar, as is very often done (*vide* article "Benzol" in Allen's "Organic Analysis," Vol. II, Pt. II). Brande describes the discovery of benzene as follows:—

"When certain oils are passed through red-hot tubes, as in the process for making gas for the purpose of illumination, there is at the same time a vapour produced, which, by considerable pressure, and by cold, may be reduced to a liquid state. Large quantities of this liquid were obtained at the Portable Gasworks by subjecting the gas produced by the decomposition of whale oil to a pressure of 30 atmospheres; this occasioned the deposition of the fluid, which was drawn off by a valve; it effervesced as it issued forth, and by the difference of refractive power, a dense transparent vapour was seen at the same time descending through the air. This effervescence immediately ceased, and the liquid was readily retained in ordinary stoppered bottles. One thousand cubical feet of good gas yielded nearly one gallon of it." It was from this fluid that Faraday separated benzol by fractional distillation.

Mitscherlich prepared benzene in 1833 by dry distillation of calcium *benzoate* and gave it its present empirical formula and also its name. Leigh claimed to be the first to discover benzene in coal-tar, but A. W. Hoffmann was the real discoverer of benzene in coal-tar, recognizing it decisively by its conversion into nitrobenzene and aniline in 1845. The method by which it could be extracted in large quantities from coal-tar was elaborated in Hoffmann's laboratory by Mansfield (British Patent No. 11,960, 11 November, 1847). Mansfield manufactured benzene on the large scale, and described very exactly the principles of dephlegmation by means of which the different hydrocarbides in coal-tar naphtha can be separated from one another, and he showed decisively that alcohol rectification plant could be used for the purpose and even more advantageously than in the case of alcohol. This suggestion is everywhere ascribed in the special literature of the subject to E. Kopp, which is untrue, because Kopp does not mention it until 1860 (Lunge). Mansfield profited by the property, previously observed by Faraday which benzene possesses, of crystallizing at 0° C., to prepare it absolutely pure.

Benzene can be heated in sealed tubes to 400° C. without alteration, but it is decomposed when passed through a porcelain tube heated to bright redness, yielding hydrogen, diphenyl, and other hydrocarbides. Distilled over metallic sodium, benzene undergoes no change. Caustic alkalis have no action on benzene. If benzene be heated at 100° C. with from four to five times its volume of concentrated sulphuric acid, it dissolves completely therein, with formation of benzene-sulphonic acid $C_6H_5HSO_3$; the liquid solution is colourless if pure benzene be used. Under the action of heat or of fuming sulphuric acid, benzene di-sulphonic acids are formed. Benzene is only slightly soluble in water, yet sufficiently so to impart its smell thereto. It is freely soluble in alcohol, ether, wood spirit, acetone, etc. It dissolves iodine, sulphur, phosphorus (warm), and fixed oils, fats, waxes, and resins readily. It is highly inflammable, and gives off equally inflammable vapours. It must

therefore be stored with care. When illuminating gas is passed through benzene its illuminating capacity is increased. Berthelot even attributed the illuminating capacity of Paris gas almost exclusively to the benzene it contains. Formerly the luminosity of coal gas was supposed to be due to substances belonging to the ethylenic series of hydrocarbides, olefins, or to the acetylenic series.

If benzene be naturally present in certain petroleums, and is also one of the products of numerous reactions, and if it, moreover, be produced by the dry distillation of numerous organic substances, yet in actual practice the benzene of commerce is elaborated from that fraction from coal-tar which distils under 100° C., generally designated as "light oils". Pure benzene is prepared by agitating the light oils in question with (1) dilute sulphuric acid, (2) water, (3) milk of lime or caustic soda lye. The oil is next digested at 100° C. with concentrated sulphuric acid (5 gallons of acid per 100 gallons of oil) for several hours to eliminate thiophene and the hydrocarbides of the ethane and ethene series, repeating the treatment until the oil ceases to cede anything to the acid, a point indicated by the oil no longer darkening the acid. The purified oil is then separated, washed with water, and again distilled, the fraction distilling over below 90° C., being collected apart, and cooled by a freezing mixture for the benzene to crystallize out. The crystals are separated from the hydrocarbides of lower melting-point by a vacuum filter. To prepare absolutely pure benzene the crystals are repeatedly re-melted, re-crystallized, and re-separated from the mother liquor, until the crystals exhibit the physical and chemical properties of chemically pure benzene. Its flash-point is 15° C.

6*b*. *Toluene*.—Chemical formula, $C_6H_5CH_3$; boiling-point, 111° C.; density, 0·8824 at 0° C., 0·8720 at 15° C.; index of refraction, 20° C. (D = 0·8656), 1·4911; molecular refraction, $p\frac{n-1}{d}$; found, 52·20; calculated, 52·3; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; found, 30·79.

Toluene (methyl benzene) was discovered in 1838 by Pelletier and Walter in the products of the condensation of rosin gas and was termed rosin-naphtha. Later Deville obtained it by the dry distillation of balsam of tolu, hence its name which was given to it by Berzelius. Mansfield discovered it in coal-tar. It also exists in a great number of mineral oils. It is extracted from coal-tar in large quantities, and if desired could be obtained on the large scale in a fairly pure condition. It is used for numerous purposes, whether in the manufacture of colours or as a solvent. It is very difficult, however, to prepare it in an absolutely pure state because it cannot be crystallized like benzene. Only one toluene can exist, and Berthelot and Rosenthiel have shown that all the toluenes from the most different sources are identical. Toluene is a colourless, mobile, refractive liquid. The odour of toluene differs slightly from that of benzene. It is, so to speak, insoluble in water, but it communicates its odour

thereto; it mixes with alcohol, ether, and carbon disulphide. It dissolves phosphorus, sulphur, iodine, resins, and oils and fats. It burns

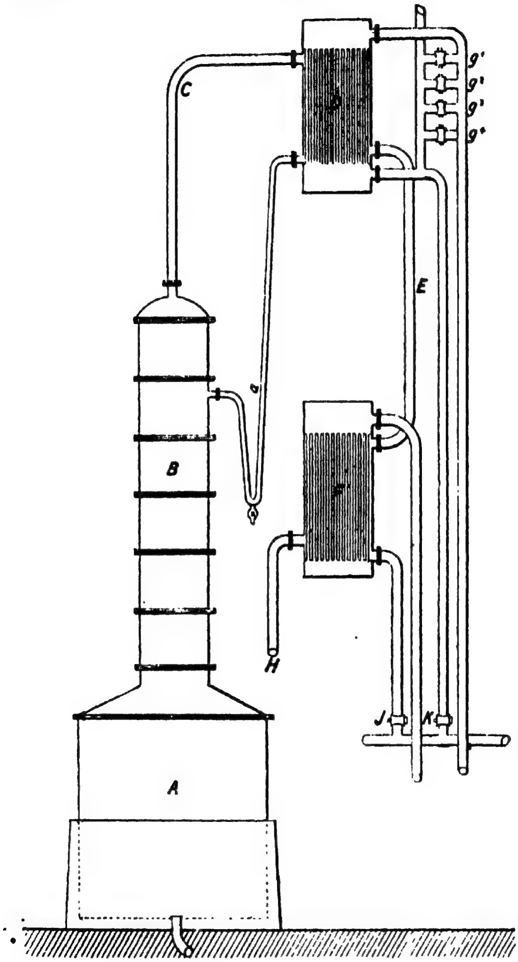


FIG. 1.—VEDLE'S TOLUENE RECTIFIER.

A, body of still; B, rectifying column; D, analyser; F, cooler; E, pipe leading uncondensed vapours from analyser to cooler; H, pipe leading distillate to receiving tanks; J, pipe leading cold water to cooler; K, to analyser.

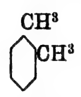
with a bright but very smoky flame. Passed through a red-hot tube it yields benzene, naphthalene, anthracene, phenanthrene. According

to Berthelot toluene possesses the property of rendering oxygen active; when it is agitated in presence of air with a lukewarm very dilute solution of indigo the liquid is decolorized. Flash-point, 15° C.

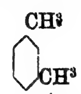
Vedle's Toluene Rectifier.—This consists of a wrought-iron double-cased still A, 6 feet deep by 6 feet wide, fitted with a perforated coil for heating the contents when required by open steam. The still is surmounted by the dephlegmating column B, which is of similar construction to the benzene dephlegmator. The vapours leaving the dephlegmator pass out by the pipe C and enter the condenser, or analyser D, which consists of a cylindrical or square copper cistern 5 feet deep by 2 feet wide, in which is fixed a number of tubes 40 inches long by 1⅛ inch in diameter. There are about sixty tubes in this analyser, and through them the condensing water passes whilst the hydrocarbide vapours fill the space around the tubes. The uncondensed vapours pass out by the pipe E and enter the cooler F of similar construction to the analyser D. The higher boiling hydrocarbides, which have been condensed in the analyser, run back through the pipe A into the rectifying column. The distillate runs from the cooler F, through the pipe H, into the receiving cisterns. The condensing water enters the cooler through the tap J, and is fed to the analyser by means of the tap K. The waste-water pipes may be easily recognized.

When the still A is charged with the residues from the manufacture of pure benzene it is first heated by means of the steam jacket, and finally wet steam is slowly admitted, the progress of the distillation being carefully regulated. When the distillate begins to run slowly, the water supply is slackened by means of the tap K until the water in the analyser D commences to boil. The distillate is collected in separate cisterns, or better in 100 gallon drums, which are numbered and separately analysed. When the distillate begins to run slowly from the cooler F, while the water in the analyser is boiling, the tap g^1 is opened. The overflow of the water now runs away through the pipe connected with the tap g, the space in the analyser above this being filled with steam. In regulating the taps g^2, g^3, g^4, each time the distillation begins to flag a mixture of toluene and xylene is distilling. At the end of the operation the tap K is completely shut and the analyser becomes filled with steam. The distillation of xylene then commences and the operation is concluded when no more comes over at 142° C. By analysing the contents of the drums the rectifier finds at once which contain pure toluene and pure xylene and which contain intermediate products.

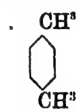
6*c*. *Xylene.*—The three dimethyl benzenes or xylenes, $C_6H_4(CH_3)_2$, viz.:



Orthoxylene



Metaxylene



Paraxylene

occur in coal-tar. Just as toluene is benzene in which one atom of hydrogen (H) is replaced by the radical methyl (CH_3), so also xylene is benzene in which two atoms of hydrogen have been replaced by methyl. Molecular weight, 106; boiling-point, 136-140° C.; flash-point, 30° C. = 86° F.

Xylene is principally produced by fractional distillation of solvent naphtha, or of the higher boiling portion of crude coal-tar naphtha, and with proper appliances there is no difficulty in obtaining it to distil within two degrees. It might be thought that a hydrocarbon boiling at its proper degree would be pure enough for all commercial purposes, and no doubt such is the case with benzene and toluene. It is, however, different with xylene, of which there are three modifications known, and of these the meta- is the only one possessing technical value. No practical use for the ortho- and para- modifications have yet been found.

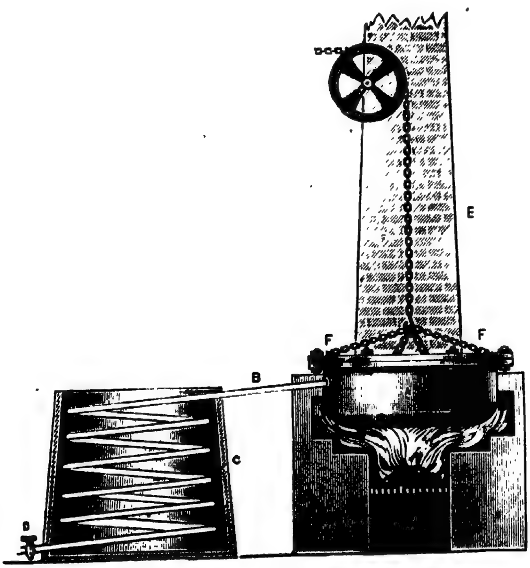


FIG. 2.—DRY DISTILLATION OF RUBBER. STILL AND CONDENSER.

7. *Cajeput Oil—Source.*—Cajeput oil is the essential oil distilled with water from the leaves of the *Malaleuca leucodendron.* *Colour.*—Its greenish colour is due to a small quantity of resinous matter. Sometimes oils which have been bleached by natural oxidation are artificially coloured green by copper salts. *Taste and Smell.*—It has

a burning taste with a strong smell of camphor, turpentine, and savin *Composition and Properties.*—It may be separated by fractional distillation into two portions: two-thirds of the liquid, having a density of 0·897, passes over between 175° C. and 178° C., and the remaining third, having a density of 0·920, between 178° C. and 250° C. *Uses.*—Its principal use in varnish-making is said to be as a solvent for Angola copal. It is also used to preserve entomological specimens and in medicine.

8. *Caoutchoucine.*—This is a product of the dry distillation of india-rubber in a specially constructed still made of iron and built into brickwork. A connecting pipe leads from the still-head to the worm in condenser C. The still has a closely fitting iron cover which may be raised or lowered at will by the overhanging chain and pulley. A hole in the cover gives passage to a thermometer by which the temperature is regulated. The process is started by raising the still-head and introducing a sufficiency of rubber cut into small pieces either by itself or along with half of its weight of crude distillate from a previous charge. The still-head is then lowered and secured with nuts and bolts as shown and the fire lighted. As the thermometer approaches 600° F. a dark liquid comes over which condenses in the worm and runs off the stop-cock D into a receiver. When the thermometer rises above 600° F. the fire is withdrawn. The crude distillate may be separated by fractionation into three liquids of different boiling-points and specific gravities, thus:—

0·67 boiling at 90° F.
0·69 boiling at 104° F.
0·92 boiling at 599° F.

Caoutchoucine is not only an excellent solvent for rubber but also for varnish resins, even copal being said to be easily soluble therein

9. *Carbon Disulphide.*—Chemical formula, CS_2; molecular weight 76; boiling-point, 46° C.; density of vapour (air = 1), 2·63; density of liquid, 1·292; melting-point, 116° C.; flash-point, 20° C.; index of refraction of vapour (air as unity at 0°, vapour of gas at 12° C.) 2·12; absolute, 1·000620.

Carbon disulphide is prepared by heating in a furnace to bright redness freshly glowed wood charcoal in large tubulated fire-clay retorts lumps of sulphur being run in from time to time. The necks of the retorts are adapted (air-tight) to large receivers which condense and intercept any uncombined sulphur. From the latter the carbon disulphide vapours pass through condensers. The crude product is very impure, containing sulphur, sulphuretted hydrogen and other compounds, all of which combine to impart to it an abominable smell, from which no amount of repeated distillation will free it. It is purified by shaking it up with mercury and mercuric chloride and subsequent distillation. The mono-hydrated sulphates of both copper and iron are also used to purify it, and do so very effectively.

When sulphide of carbon is left for twenty-four hours in contact with ½ per cent of its weight of finely powdered corrosive sublim-

TABLE VI.—DENSITY OF SOLUTIONS OF SULPHUR OF VARIOUS STRENGTHS PER CENT IN CARBON DISULPHIDE.

Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.
1·271	0	1·296	6·0	1·321	12·1	1·346	18·1	1·371	25·6
1·272	0·2	1·297	6·3	1·322	12·3	1·347	18·4	1·372	26·0
1·273	0·4	1·298	6·5	1·323	12·6	1·348	18·6	1·373	26·5
1·274	0·6	1·299	6·7	1·324	12·8	1·349	18·9	1·374	26·9
1·275	0·9	1·300	7·0	1·325	13·1	1·350	19·0	1·375	27·4
1·276	1·2	1·301	7·2	1·326	13·3	1·351	19·3	1·376	28·1
1·277	1·4	1·302	7·5	1·327	13·5	1·352	19·6	1·377	28·5
1·278	1·6	1·303	7·8	1·328	13·8	1·353	19·9	1·378	29·0
1·279	1·9	1·304	8·0	1·329	14·0	1·354	20·1	1·379	29·7
1·280	2·1	1·305	8·2	1·330	14·2	1·355	20·4	1·380	30·2
1·281	2·4	1·306	8·5	1·331	14·5	1·356	20·6	1·381	30·8
1·282	2·6	1·307	8·7	1·332	14·7	1·357	21·0	1·382	31·4
1·283	2·9	1·308	8·9	1·333	15·0	1·358	21·2	1·383	31·9
1·284	3·1	1·309	9·2	1·334	15·2	1·359	21·5	1·384	32·6
1·285	3·4	1·310	9·4	1·335	15·4	1·360	21·8	1·385	33·2
1·286	3·6	1·311	9·7	1·336	15·6	1·361	22·1	1·386	33·8
1·287	3·9	1·312	9·9	1·337	15·9	1·362	22·3	1·387	34·5
1·288	4·1	1·313	10·2	1·338	16·1	1·363	22·7	1·388	35·2
1·289	4·4	1·314	10·4	1·339	16·4	1·364	23·0	1·389	36·1
1·290	4·6	1·315	10·6	1·340	16·6	1·365	23·2	1·390	36·7
1·291	4·8	1·316	10·9	1·341	16·9	1·366	23·6	1·391	37·2
1·292	5·0	1·317	11·1	1·342	17·1	1·367	24·0		
1·293	5·3	1·318	11·3	1·343	17·4	1·368	24·3	Saturated	
1·294	5·6	1·319	11·6	1·344	17·6	1·369	24·8		
1·295	5·8	1·320	11·8	1·345	17·9	1·370	25·1		

ate, care being taken to shake or stir up this mixture, the mercurial compound combines with the substances which are the cause of the fœtid odour of this substance, and an insoluble compound is deposited. The liquid is carefully decanted, and, after 0·02 of its weight of a pure inodorous fat has been added (no reason is given for this addition), the sulphide is re-distilled with care by the heat of a water-bath. The sulphide thus obtained exhibits an ethereal odour, and is eminently suitable for the extraction of oils, fats, etc., from various substances, since, on evaporation of the purified sulphide, these matters are obtained in as fresh and pure a state as if the oils had been obtained by pressure.

Properties.—Carbon disulphide is a transparent, colourless, and highly volatile liquid of great refractive and dispersive power. Its taste is pungent and aromatic, and its smell when pure is similar to chloroform. Its density at 15° C. is 1·27, and it boils at 46·5° C. It burns with a blue flame yielding sulphurous and carbonic anhydrides. Its vapour when mixed with air is explosive. The technical applications of carbon disulphide are many and varied; it is an excellent solvent for oils, fats, and resins, wax and paraffin, and for sulphur (see Table VI). In virtue of the latter property it is much used in the manufacture of vulcanized caoutchouc, i.e. india-rubber partly saturated with sulphur. It is extensively employed in the extraction of

oil from seeds, and of grease from wool. Carbon disulphide dissolves dammar and rosin well, but elemi, sandarach, and mastic with difficulty. It does not dissolve shellac or amber and merely causes copal to swell.

But the use of carbon disulphide as a solvent for resins in varnish-making is greatly restricted by the fact that air containing a small quantity of the vapour has the same toxic effects as chloroform, producing insensibility. In large quantities it is poisonous. But some authorities ascribe the toxic effects of carbon disulphide to congestion of the brain caused by the intense cold produced by its evaporation. Moreover, there is the further risk of fire or explosion. Carbon disulphide is not miscible with water, and when agitated with iodine or bromine water it absorbs the halogen and acquires a faint purple or brown-red colour, as the case may be. The smell of carbon disulphide should not be repulsive nor fetid. It should give no dark turbidity with a solution of acetate of lead, nor be either acid or alkaline. Alcohol may be detected by the lower density and by the diminution in volume when the sample is shaken up with equal volumes of glycerine or water. Owing to its higher density and non-miscibility with water, it is possible to store it under water, which should always be done to avoid risk of fire or explosion.

10. *Carbon Tetrachloride.*—Chemical formula, CCl_4; molecular weight, 153·8; boiling-point, 8° C.; non-inflammable; density, 1·629; index of refraction, 1·45789.

Carbon tetrachloride may be prepared in the laboratory in various ways, but the best method is that of Kolbe. A mixture of chlorine and the vapour of carbon disulphide is passed through a porcelain tube filled with fragments of porcelain, and, at a high red heat, sulphur chloride and carbon disulphide are formed which produce a deep reddish-yellow liquid condensable in a well-cooled receiver. The chlorine is best saturated with the vapour by merely passing it through a flask containing carbon disulphide, which is sufficiently volatile to be carried off in adequate quantity by the chlorine current. The flask should not be heated, as in that case the excess of the vapour is washed. The red liquid is left for some time in contact with a strong solution of caustic potash and occasionally shaken, which absorbs the chloride of sulphur so that the carbon tetrachloride may be distilled off from the mixture. This heavy liquid solvent may also be prepared by the action of chlorine on ordinary methylic chloride or on chloroform. Its vapour density is 5·3 that of air. It is soluble in alcohol and ether but not in water.

On the large scale, the manufacture of the tetrachloride is carried out by different methods, the starting-point of which is always carbon disulphide, on which chlorine is caused to react in either a direct or an indirect manner. Direct action only occurs at a high temperature, or in presence of a contact body. Working indirectly, chlorine is made to react in the form of a compound, such as sulphur chloride, whether directly, or, better still, with a contact body. Cote has

elaborated a process by which carbon tetrachloride may be manufactured continuously in a closed vessel. The contact substances employed are manganous chloride for the formation of sulphur-chloride and iron-sulphide for the reaction of sulphur-chloride on carbon disulphide. The plant consists of a column No. 1 filled with coke impregnated with manganese chloride. The carbon disulphide enters it by a small central tube, and reverses towards the top; the chlorine enters from below. Sulphur chloride is formed in this column, and also carbon tetrachloride. The mixture flows into another column No. 2 filled with coke impregnated with iron sulphide. There it meets a current of carbon disulphide from the bottom of No. 2. Carbon tetrachloride is formed, mixed with a little sulphur chloride, and holding sulphur in solution. The mixture is passed to a third column No. 3 filled with metallic iron and heated to 120° C. The liquids carbon tetrachloride and sulphur chloride are instantaneously vapourized and pass to the rectifier; the sulphur which was dissolved melts and runs into a furnace heated electrically and in which carbon disulphide is produced. The rectified tetrachloride from the rectifier passes to the purifier, where it is distilled in the presence of water to remove the last traces of sulphur chloride. It flows afterwards after cooling into the coil K. The carbon disulphide produced in the furnace returns to the bottom of the column and recommences the cycle. The electric heating in the furnace was adopted because it allowed the heat to be better utilized, and because the manufacture appeals particularly to the electrolytic soda industries, enabling them to utilize, in an interesting form, part of the chlorine which they produce.

The special advantages of carbon tetrachloride over carbon disulphide, benzine, petroleum spirit, as a solvent are (1) its uninflammability; (2) its low latent heat of vaporization, hence fuel economy where it is used as an oil, fat, or resin extractor; (3) its ready condensation, consequently less loss in its industrial use; (4) its great solvent power. This solvent, as is well known, quickly corrodes iron, and therefore all the vessels, coils, tanks, and fittings must be lined with lead, or, preferably, tin. But lead lining is costly and tinning doubles the cost of the apparatus.

The corrosion of metallic vessels by carbon tetrachoride has been the subject of numerous investigations. This corrosion is more in evidence in the presence of water. The best vessels to use in descending order are: galvanized wrought-iron, copper, cast-iron, tinned-iron, brass, sheet-iron. Galvanized-iron may be used for the inside of the vessels, the piping of copper and lead, and the taps and valves of bronze.

11. *Chloroform.*—$CHCl_3$; molecular weight, 118·5; boiling-point, 61° C., 141·75; density, 1·500; vapour density, 4·19; index of refraction, α[D], 1·4490. Chloroform is made by distilling a mixture of alcohol and bleaching powder and rectifying the distillate. It is very volatile even at ordinary temperatures, producing by rapid

evaporation great cold, but leaving neither a residue nor a film of moisture, nor any unpleasant odour when wholly evaporated by the warmth of the hand by waving it to and fro in a porcelain basin. Ten parts of chloroform dissolve in 7 of rectified spirit, 1 in 1½ of ether, and 1 in 200 of water. It burns only with a wick; the vapour is toxic, but not explosive. It is miscible in all proportions with absolute alcohol, ether, benzol, carbon disulphide, and essential and fatty oils, and is an extensive solvent for resins, acting on vulcanite, and dissolving caoutchouc, gutta-percha, paraffin, camphor, mastic, elemi, tolu, benzoin, and copal—amber, sandarach and lac are only partially soluble.

12. *Other Chlorine Derivatives.*—The following series of solvents, hitherto unavailable for technical purposes, are now on the market as fulfilling the above conditions. They are all chlorine derivatives of ethane or ethylene, prepared from electro-chemical acetylene and chlorine, the fundamental material being acetylene tetrachloride (symmetrical tetrachlorethane). They are arranged below in the order of their boiling-points, the densities being also added:—

TABLE VII.—BOILING-POINT AND DENSITY OF CHLORINE DERIVATIVES USED AS SOLVENTS.

		Boiling-point.	Specific Gravity.
Ethylene dichloride (sym.)	$C_2H_2Cl_2$	55 C.	1·25
Ethylene trichloride .	C_2HCl_3	88 C.	1·47
Ethylene perchloride .	C_2Cl_4	121 C.	1·62
Tetrachlorethane (sym.) .	$C_2H_2Cl_4$	147 C.	1·60
Pentachlorethane . .	C_2HCl_5	159 C.	1·70
(Hexachlorethane) . .	C_2Cl_6	solid	—

Hexachlorethane sublimes at 185° C., it has a smell resembling camphor, and is suitable as a camphor or naphthalene substitute, etc. The relatively high volatility of this substance enables it to act energetically, without the smell being so troublesome as that of camphor or naphthalene. It is claimed for the above liquids that they are all very stable and inert solvents, and the wide range of boiling-points they present renders them suitable for a large number of purposes. Being all uninflammable they preclude the risk of explosion in use. The three ethylene derivatives have, it is claimed, practically no action on iron, copper, lead, or zinc even in presence of moisture, nor do they react on acids or alkalis, fats or oils, either alone or in presence of metals. From a technical standpoint their behaviour toward wrought-iron is particularly important, the extent of the corrosion being extremely minute (ratio about 0·002 : 7·6 as compared with pure carbon tetrachloride). They also attack lead to a smaller extent than the solvent last named.

The most suitable as an extractive agent is ethylene trichloride, which boils at very near the same temperature as benzene, and is very little dearer, bulk for bulk, than carbon tetrachloride. When used in wrought-iron vessels it extracts fats so as to yield a product equal to that extracted with benzol. It is perfectly inodorous, and can be

readily distilled, without residue, by the aid of steam, so that the loss in working is very small. The heat of evaporation is about 16·35 cal. per lb., or one-tenth that of water. At indoor temperature its solubility in water is about that of carbon tetrachloride; and it presents the additional advantage of being perfectly innocuous to health, there being no narcotic action such as is exhibited in a high degree by chloroform and carbon tetrachloride. The dichloride and perchloride of ethylene resemble the trichloride in their solvent power, the first-named forming a useful substitute for ether.

Tetrachlorethane also has a high solvent action on fats, oils, and resins, and it may be used instead of chloroform for dissolving cellulose acetate in the manufacture of artificial silk. As a solvent for sulphur it has no equal, and it is miscible with this substance in all proportions at temperatures above about 120° C., redepositing the whole of the dissolved sulphur, with the exception of about 1 per cent, in a finely crystalline state on re-cooling to ordinary temperature. Pentachlorethane has similar properties, and is used for dissolving the varnish resins as well as for the extraction of fats. Both these solvents will also dissolve chlorine without undergoing any change, the tetrachloride taking up about thirty times its own volume of the gas, on which account it is useful in chlorination processes.

Tetrachlorethane and pentachlorethane, though attacking wrought-iron in the presence of moisture, are, it is claimed, inert toward cast-iron; but they react on alkalis, with liberation of hydrochloric acid.

Care should be taken in the use of all chlorine derivatives as they are all more or less anesthetic. Varnishes made from them should be made and applied in a well-ventilated atmosphere.

13. *Dichlorhydrine.*—$CH_2Cl \cdot CH(OH) \cdot CH_2Cl$; density, 1·37.

Preparation.—Glycerine is mixed with fifteen times its weight of fuming hydrochloric acid, and the mixture heated, for eight hours, to 100° C. To extract the dichlorhydrine formed, the product is agitated with carbonate of soda and ether. After evaporating the ethereal solution the residue is distilled, collecting what distils about 228° C. This distillate is treated with lime and ether. Dichlorhydrine is obtained after evaporation of the ether. Dichlorhydrine has the appearance of an oil, has an ethereal odour and boils at 178° C. Caustic potash separates potassium chloride from it even in the cold. Heated for a long time with an excess of hydrochloric acid dichlorhydrine is converted into epichlorhydrine.

14. *Epichlorhydrine.*—C_3H_5ClO; density, 1·194 (at 11° C.).

Preparation.—This substance was discovered by Berthelot. A mixture of 5 volumes of glycerine (properly dried) with 1 volume of glacial acetic acid is saturated with hydrochloric acid gas, after which it is distilled, collecting what passes between 180° and 220° C. It is a mixture of dichlorhydrine and aceto-dichlorhydrine, which is converted into dichlorhydrine and acetate by the action of caustic potash. To 500 c.c. of this mixture a tepid concentrated solution of 350 grammes of caustic potash is added, stirring and allowing to cool

TABLE VIII.—SHOWING SOLVENT ACTION OF EPICHLORHYDRINE AND DICHLORHYDRINE ON THE DIFFERENT VARNISH RESINS AND THE NATURE OF THE COAT OF VARNISH PRODUCED.

Resin.	Epichlorhydrine.	Dichlorhydrine.
Elemi	Freely and completely soluble, both in the cold and in the hot, forming yellow to greenish solutions which leave a bright tacky coat on evaporation.	Freely and completely soluble. The solution turns brown when warmed.
Mastic	Freely and completely soluble in the cold or in the hot. Solution pale yellow, leaving a lustrous, colourless coat on evaporation.	Not so freely soluble. The solution turns brown on warming.
Dammar	Imperfectly soluble, more readily so in the warm. The bright yellow filtrate gives a hard, solid, bright coat of varnish.	Dissolves fairly freely to a brown solution in the cold. When warmed colour changes to deep brown-violet.
Courbaril Copal	Imperfectly soluble in the cold, almost entirely so in the warm, to a bright yellow varnish.	Perfectly soluble in the cold to a yellow solution which turns brown when warmed.
Dragon's Blood	Readily soluble, except a brown residue. The solution is blood-red, but gives a bright layer of varnish.	Imperfectly and less readily soluble; solution yellowish-red in colour.
Sandarach	Imperfectly soluble in the cold or hot. Solution, pale yellow.	Dissolves perfectly in the cold to a brownish-yellow solution, becoming deep brown when warmed.
Bleached Shellac	Sparing soluble, imperfectly so even in the warm.	Readily and perfectly soluble in the warm. Solution yellowish. Does not turn brown. Dries very slowly.
Zanzibar Copal	Partially soluble in the cold, freely in the hot. Solution pale yellow and gives a hard, bright coat.	Partially soluble in the hot, to a brownish solution, turning dark brown when heated.
Angola Copal	Partially soluble in the cold, more readily in the hot. The faint yellow solution gives a hard coat of varnish.	More readily soluble; solution turns brown when warmed.
Manila Copal	Partially soluble in the cold, the insoluble portion swelling up to a gelatinous mass almost completely soluble in the warm; gives a yellow solution and hard coat of varnish.	The greater part soluble in the cold. The brownish-yellow solution turns brown when warmed.
Kauri	Partially soluble in the cold (the remainder swelling up). Perfectly soluble in the hot.	Almost perfectly soluble to brownish-yellow solution which turns brown when warmed.
Amber	Partially and very slowly soluble; solution yellow.	Sparingly soluble. The lumps of amber turn brown when heated.
Asphaltum	Very sparingly soluble cold or hot.	Very sparingly soluble cold or hot.

after each addition. After an hour or two the oily layer which floats on the surface is decanted and distilled, collecting what passes below 165° C. The product is purified by fractional distillation, collecting what passes about 120° C. Epichlorhydrine is formed, in this reaction, at the expense of the dichlorhydrine, from which the potash removes the elements of hydrochloric acid.

Epichlorhydrine is especially suitable for the production of very hard negative varnishes, which will permit of retouching. Dichlorhydrine, on the other hand, gives a brown coat of varnish, and not a colourless one like epichlorhydrine. This is true with all resins except bleached shellac. For this dichlorhydrine is a better solvent than epichlorhydrine. Neither dissolves asphaltum well.

Valenta recommends especially quick-drying copal varnishes made with epichlorhydrine, which gives a hard, colourless coat, and take retouching excellently. He gives the two following recipes for such varnishes:—

(*a*) Dissolve 20 grammes of Manila copal in 70 grammes of epichlorhydrine on the water-bath. On solution add 100 c.c. of absolute alcohol and filter. This varnish can be diluted at will with a mixture of one part epichlorhydrine and five of alcohol, and can be used either on warm or cold plates.

(*b*) Pale Angola copal is digested in small pieces with four or five times its weight of epichlorhydrine on the water-bath. After half an hour double the volume with absolute alcohol, and complete solution will take place; then filter. Dilute, if required, with alcohol.

These varnishes give very hard, brilliant coats, which stand damp very well.

CHAPTER IV.

SOLVENTS (*CONTINUED*)—ALCOHOL, ETHER, AND ETHEREAL SALTS.

15. *Ethylic Alcohol, Common Alcohol.*—On the water type a molecule of water H_2O in which 1H is replaced by ethyl, thus, C_2H_5HO; molecular weight, 46; density at 0° C. = ·8002; solidification-point, − 130° C.; boiling-point, 78·4° C.; solubility in water and ether, ∞; index of refraction at 15° C. $\left(d^t_4\ 0{\cdot}7975\right)$, 1·3628; at 10° C. $\left(d^t_4\ 0{\cdot}8095\right)$, 1·36363; at 20° C. $\left(d^t_4\ 0{\cdot}7910\right)$, 1·35960; molecular refraction, $p\frac{n-1}{d}$; found, 20·73; calculated, 20·6; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; found, 12·71; calculated, 12·78.

Ethylic alcohol is the principal spirit obtained from fermented liquors, such as wine, beetroot juice, fermented grain-worts, etc., by distillation. The term principal spirit is used advisedly, as will be seen in the sequel. Ordinary unrectified grain spirit is a highly impure product indeed, and our excise laws do not admit of continuous working to produce a pure product at all approaching the chemically pure alcohol available on the Continent. Our distillers are State-aided to work intermittently and State-aided to continue to work with obsolete plant. The user of such spirit is not considered. For a good many years the distilling plant employed, more especially on the Continent, has been so perfected that by a single distillation an alcohol of 95 per cent strength free from fusel oil (amylic alcohol), aldehydes, acids, etc., may be obtained. Alcohol being more volatile than water, when a mixture of the two is distilled in a pot still by the intermittent system, the alcohol comes over first, mixed with a certain quantity of water. When these vapours are condensed just as they are given off by the liquid subjected to distillation a spirituous liquor is collected, the strength of which depends upon how far the distillation process has been carried. The longer the duration of distillation, the weaker the spirit. In any case, the alcohol is too weak for industrial use. Redistilled in a rectifying still only the middle runnings are at all anything like approaching purity.

But, if instead of condensing the vapours *per decensum* we cause them to ascend into a series of receivers arranged the one above the other, or into a column (Fig. 1) containing receptacles at different

heights to receive the condensed liquid, it is clear that the vapour of water will condense first and nearest to the still A in which the worts, etc., are being heated, and to which this condensed liquid is constantly being returned, whilst the alcoholic vapours, on the other hand, will rise and ascend farther and farther away from the source of heat towards the cooler portions of the column where the more readily condensable vapour of water cannot follow them. Finally the alcoholic vapours are themselves condensed in the cooled condenser F most distant from the still. But those portions which condense first are more dilute and impure than the portions which condense farther away. Only this latter portion is collected after purification for sale, the more watery portions charged with last running impurities flow back into the heated parts of the column where they are again deprived of their more volatile constituents. The alcohol in the foreshot of the pot still and intermittent stills, generally abounds in aldehydes and ethers and the last runnings in fusel oil. In the continuous rectification distillation columns there is (1) a continuous feed of raw spirit running into the still, and continuous separate elimination, each from its appropriate condenser of (*a*) ethers and aldehydes, (*b*) pure alcohol, (*c*) fusel oil, and (*d*) water. But for particulars regarding continuous distillation plant and further particulars on the distillation and rectification of alcohol generally, see McIntosh's "Industrial Alcohol" (Scott, Greenwood & Son).

Absolute Alcohol is prepared by rectifying the alcohol of commerce by substances which take up water. Quick-lime is the substance most generally used. The alcohol is digested with a large quantity of quick-lime in a flask for two days. The latter is then connected with a Liebig's condenser and the alcohol is distilled off. The quick-lime does not appear to slake much. The first and last portions are rejected because, even when working with almost absolute alcohol, the former contains a large proportion of water; whilst, on the other hand, owing to the high temperature the last portion is apt to contain water extracted from the calcium hydrate by the absolute alcohol. These two portions being collected apart the remainder is absolute alcohol; potassium permanganate does not redden it but imparts a faint brown tint.

Instead of directly distilling the alcohol through a Liebig's condenser, the flask may be attached to a vertical reflux condenser, and boiled on the water-bath for an hour, when the condenser is changed to the ordinary position and the alcohol distilled off as before; in this case the lime, some lumps of which should originally have projected above the surface of the liquid, is completely disintegrated. Care must be taken not to use too much alcohol, as the heat generated by the slaking of the lime may cause such sudden and violent ebullition as to project a mixture of alcohol and lime through the condenser.

Where the alcohol originally contained more than 5 per cent of water, a single rectification is not enough, and less quick-lime must be used, otherwise the flask may be broken by the heat developed in

slaking. Better results are obtained by digestion with, and distillation over, caustic baryta, made by decomposing the nitrate.

Metallic sodium has been used to remove the last traces of water. A small piece is dissolved in the alcohol, and the whole distilled at a steam heat. The sodium forms ethylate of sodium with disengagement of hydrogen, whilst the traces of water which the alcohol contains decompose the ethylate with the formation of caustic soda and alcohol.

$$\left.\begin{matrix}Et\\Na\end{matrix}\right\}O + H_2O = NaHO + EtHO$$

Sodic Ethylate, Water = Caustic Soda, Alcohol

But, according to Mendelejeff, when either sodium or sodium amalgam is used to dehydrate alcohol, traces of sodium or sodium and mercury are found in the distillate. Potassium carbonate has been used, but it is too weak a dehydrating agent.

A very pure absolute alcohol is obtained on the large scale by simple filtration through quick-lime. Any convenient apparatus may be used, such as an inverted two-gallon tin can, the bottom being removed and a lid tightly fitted in its place, the cylindrical part of the can being lined inside with a cylindrical perforated vessel, in the centre of which a tube is fixed. The can acts as a jacket. The inner vessel is filled with quick-lime and as much alcohol as it will hold. The central tube communicates with the interior of the jacket. The inverted neck of the can is fitted with a stop-cock for running off the dehydrated alcohol after being left in contact for fourteen days.

In the manufacture of absolute alcohol as conducted by Squibb by very slow, cold percolations through large successive portions of quick-lime, it not infrequently comes from the rectifying still of a specific gravity below that of the lowest tables and of the best and most recent authorities, and the entire product of the process for years has been of such strength that all the hydrometers tried have sunk below the reading scale. A U.S.A. Government inspector pronounced the alcohol to be 102 per cent strong. Another inspector made it 99 8 per cent, but he could not possibly have done this with his official instruments because his hydrometer would sink below the reading scale. Quite recent experiments seem to show that this exceptionally low gravity is due to etherification of the alcohol by the lime. Some further interesting particulars on the preparation of absolute alcohol are given in "Industrial Alcohol" by J. G. McIntosh, pp. 13, 14 (Scott, Greenwood & Son). The effect of the dilution of alcohol on the vapour tension of the varnish is to lower it and thus diminish speed of evaporation *pro rata.*

Properties.—Alcohol is a colourless mobile neutral liquid, possessing an agreeable spirituous odour, burning with a blue flame and without smoke. Its density according to Kopp is—

Deg. C.	
0°	0·8095
15·5°	0·7939
20·0°	0·7920

Under the normal atmospheric pressure, alcohol boils at 78·4° C. It mixes in every proportion with water. The mixture takes place with disengagement of heat, and there is a contraction after cooling. The maximum of contraction takes place when 52·3 volumes of alcohol are mixed with 47·7 volumes of water. The result only measures 96·35 instead of 100. Alcohol exposed to the air attracts moisture; it also abstracts moisture from organic substances. Placed in contact with certain salts containing water of crystallization it dehydrates them.

Alcohol is miscible in all proportions with most liquid bodies, with the exception of the fatty oils which it only dissolves in very limited proportion—castor oil and croton oil excepted, both of which it freely dissolves. In fact, next to water, it is the most extensive and important solvent. Its solvent action on resins, balsams, camphor, etc., is well known.

Adulterations.—Water may be detected by adding anhydrous sulphate of copper, which changes from greyish-white to blue in dilute alcohol. Also by permanganate of potash, which under like circumstances turns red. But these reactions fail to detect minute traces.

Slight traces may be detected by adding a small amount of the alcohol to be tested to a saturated solution in absolute alcohol of liquid paraffin. Small traces of water turn the liquid turbid at once (Crismer).

Permanganate test for foreign organic impurities in general: Ten c.c. of the absolute alcohol to be tested; 1 c.c. of water and 1 c.c. of permanganate solution give a red liquid which should not turn yellow before twenty minutes have expired. Cazeneuve takes chemically pure alcohol of 93 per cent and potassium permanganate solution of 1 in 1000. Ten c.c. of the pure alcohol require five minutes at the ordinary temperature to give a rather yellowish-pink colour with 1 c.c. of the permanganate solution, thus showing that the reduction is not quite complete. If an alcohol of 93 per cent shows a quicker reduction, this points without doubt to impurities. But it is urged against the permanganate test that it shows not only the presence of fusel oils but of every trace of organic matter absorbed from the barrels, bunges, and chives, and such impurities are unavoidably present in all alcohols. A slight reduction, therefore, it is pleaded, should not cause rejection. Inferior spirits show a short permanganate test, the better the spirits the longer before the permanganate is reduced.

Furfurol.—Add to 10 c.c. of the alcohol 10 drops of aniline oil and 2 or 3 drops of hydrochloric acid. If furfurol be present a more or less pinkish-red colour is produced.

Amylic alcohol.—Fusel oil may be detected by agitating 5 c.c. of the alcohol to be tested with 6 c.c. of water and 15 to 20 drops of

chloroform. The chloroformic solution is decanted and evaporated leaving the fusel oil; about 0·05 per cent may be detected in this manner. The presence of a large amount of fusel oil in commercial spirits of wine can also be detected by the turbidity formed on dilution with water. If on dilution with a large quantity of water drops separate out, acrolein should be tested for by adding an equal amount of concentrated sulphuric acid and caustic potash solution. If acrolein be present it is recognized by its smell. If 3 drops of concentrated hydrochloric and 10 drops of aniline oil give a fine raspberry colour, amyl alcohol is present.

Free Acid in Alcohol.—The spirit varnish-maker does not give this important question the attention it deserves, nay, he even introduces oxalic acid to accentuate the evil effects of free acid and thus adds fuel to the fire. In fact the unrectified spirits furnished by the ordinary distilling columns are far from being a mixture of water and pure alcohol. Amongst the substances which deteriorate them the following may be mentioned: Propylic, butylic, isoamylic, and hexylic alcohols, the aldehydes of ethylic and homologous alcohols, acetone, glycols, acrolein, furfurol. The acids produced by the oxidation of these different alcohols, or from the reduction of pre-existing acids, pelargonic acid, etc. The ethers (esters or ethereal salts) produced by all the possible combinations of all these alcohols with the aldehydes, essential oils, etc. Is it a matter of wonder therefore when varnish is made from such crude acid charged alcohol that it should corrode the metal of the tinned vessel in which it is packed, attacking first the solder and then by a kind of catalytic action the tin itself? The lead in the solder thus forms a lead acetate which gives a violet "laccate" with an alcoholic solution of shellac. Now the function of the oxalic acid added by the spirit varnish-maker is to form lead oxalate from the violet lead laccate and so set free the colouring matter from the lead in a bleached condition. But the varnish-maker always uses far too much oxalic acid, and his spirit varnish instead of being a protective agent becomes a corrosive one when applied on metals. According to Schweissinger, 0·4 c.c. $\frac{n}{10}$ soda solution was required to neutralize the free acid in a good alcohol. But good alcohol should not turn blue litmus red. The varnish-maker should insist on being supplied with perfectly neutral alcohol (see p. 33). This free acid and other impurities in ordinary alcohol are fruitful causes of blooming and countless other defects in varnishes. It is manifestly absurd to cry out for pure alcohol free from wood spirit, etc., and mineral oil only to rest satisfied with an impure grain spirit saturated with fusel oil, and nearly if not quite as impure as the ordinary wood spirit itself. The above list of impurities tells its own tale. But it will suffice perhaps to call attention to it for varnish-makers no longer to rest satisfied with whatever grade of spirit the distiller chooses to send them, too often a mixture of first and last runnings. Too often the only tests applied by spirit varnish-makers are the sight

and the smell; if the alcohol be fairly clear and does not smell outrageously it is passed for use, and far too often with highly detrimental results. The following is the analysis of an alcohol rectified at the rate of 176 gallons per hour (!) in Barbets' continuous distillation rectification still:—

Acids—Nil.	Colour—Transparent like water.
Aldehydes—Nil.	Odour—Fine.
Savalle's test—Colourless.	Taste—Pure.

Were a specification framed on lines similar to the above by our excise and insisted on for all industrial alcohol receiving State aid, the policy would be more sound than now, when the production of an impure, grain, or molasses alcohol is fostered by extraordinary grants, which if our fiscal policy was on continental lines as regards potable alcohol need never have been instituted.

The above analysis proves that the continental user of alcohol has a perfectly pure spirit available. The result of the recent departmental committee was merely to restrict the amount of impurities in the denaturant. There has been no improvement in the spirit itself. No wonder that British varnish-makers can match spirit varnishes in their depots abroad with foreign pure alcohol, but not with the alcohol to be got at home. Even in countries where the manufacturing processes are under the rigid chemical control of the fiscal authorities, as in Switzerland, where alcohol is a Government monopoly, the alcohol contains free acid; of 1070 analyses the maximum of $\frac{n}{20}$ soda solution used was 3·2 c.c. and the minimum 0·5 c.c. How much worse must be the industrial alcohol produced in Great Britain where there is no chemical control whatever. Our excise only trouble themselves to see that the wood spirit for methylation is sufficiently nauseous. It seems, however, scarcely too much to ask that at least the "pure" alcohol supplied for industrial purposes should be tested by the excise as to whether it is chemically pure or not.

16. *Ether* (Sulphuric Ether, Ethyl Ether).—Chemical formula, $(C_2H_5)^2O$ (looking at it, as built upon the water type, it may be regarded as water H_2O in which the two atoms of hydrogen in the water have been replaced by two of ethyl); molecular weight, 74; boiling-point, 35° C. (95° F., blood heat); freezing-point, $-117°$ C.; flash-point, $-20°$ C.; solubility in water, 1 in 12; in alcohol, in all proportions; index of refraction at 15° C. $\left(d^{t}_{4}\ 0·713\right)$, 1·3573 Kundt; 1·3554 Gladstone.

Ether is made by distilling a mixture of sulphuric acid and alcohol. The alcohol is continuously fed into hot sulphuric acid. In the first reaction sulphovinic acid and water are first formed, thus:—

$$C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

Then the fresh alcohol acts on the sulphovinic to form ether and sulphuric acid. The process is thus continuous:—

$$C_2H_5HSO_4 + C_2H_5HO = (C_2H_5)^2O + H_2SO_4.$$

A detailed illustrated description of the *manufacture* of ether is given in McIntosh's "Industrial Alcohol".

Ether is the *beau ideal* of an all-round volatile solvent. It evaporates very readily and can be easily and rapidly distilled from a hot water-bath, leaving a residue free from any odour or coloration due to the solvent whatsoever. Its vapour mixed with air is *highly explosive*, and being very diffusible will run 12 feet from its source to a flame. This drawback restricts its use except for photographic varnishes.

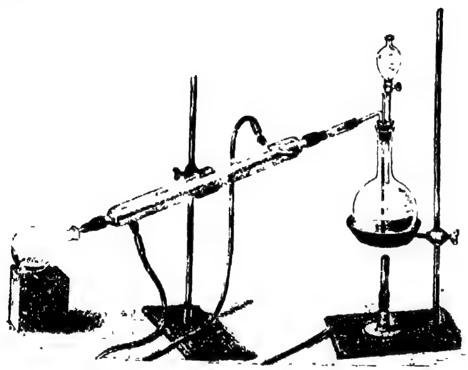


FIG. 3.—APPARATUS FOR PREPARATION OF ETHER.

Retort stand supporting flask containing mixture of alcohol and sulphuric acid fitted with a separating funnel dipping into flask and continuously feeding it with alcohol and with Liebig's condenser leading to receiver.

17. *Ethyl Acetate.*—Chemical formula, $C_2H_5C_2H_3O_2$ (built on type of potassium acetate $K_2C_2H_3O_2$, the potassium (K) being replaced by ethyl C_2H_5); molecular weight, 88·1; density at 0° = 0·924; boils at 77·15; solubility in water, 9 per cent; index of refraction, n for H_2 (density of sample tested at 20° C. = 0·9007), = 1·37068; molecular refraction, $p\frac{n-1}{d}$; found, 36·22; calculated, 36·6; molecular refraction, $p\frac{n_2-1}{(n_2+2)d}$; found, 22·14; calculated, 22·16.

Ethyl acetate (acetic ether), discovered in 1759 by the Count de Lauraguais, is met with, already formed, in wine or in wine vinegar. It is used technically as a solvent in making smokeless powder in celluloid manufacture and in collodion and celluloid varnish manufacture where it replaces amyl acetate. It is prepared by the action of acetic acid on alcohol, but, as etherification by an organic acid is accomplished slowly and incompletely, it is preferred to manufacture ethyl acetate by the intervention of a mineral acid, like sulphuric acid, which is made to react on the acetate of soda and the alcohol. Many

different recipes have, however, been given, amongst others those in the following table. Small quantities of sulphuric acid and alcohol, previ-

TABLE IX.—FORMULÆ USED IN MAKING ACETIC ETHER.

	A	B	C	D	E	F	G	H
Acetic acid	—	—	—	—	—	—	63	—
Potassic acetate	3	—	-	—	—	—	—	—
Sodic acetate	—	6	6	10	-	—	—	12⅜
Plumbic acetate	—	—	—	—	6	32	—	—
Sulphuric acid	3	9	15	7	3	10	17	10
Alcohol	2	3·6	6	8	2	9	100	10

ously mixed, are run into a retort heated by steam and containing crystallized sodium acetate; heat is then applied, the liquid distils, and, after passing through a condenser, is collected in a receiver. The distilled product is then agitated with twice its volume of water rendered slightly alkaline; it is then allowed to settle, and the ethyl acetate floating on the top decanted and digested over calcium chloride before being rectified. The chloride of calcium being soluble in this acetic ether, bumping occurs in the still to such an extent as to render the operation a difficult one. It is therefore preferable, as indicated by Berthelot, to wash the crude product with a weak alkaline solution, then, after rectification, to agitate it with a saturated solution of common salt, dry over carbonate of potash, and finally rectify afresh. The wash waters, containing dissolved acetic ether and alcohol which has escaped the reaction, are fractionally distilled; the liquid, containing the acetic ether and the alcohol, is collected and used in a fresh operation. Ethyl acetate, the boiling-point of which is 74° C. (165·2° F.), is a colourless, very mobile liquid, lighter than water; it has a very pleasant ethereal odour, is slightly soluble in water (1 in 7), and the solution is decomposed by potash with formation of potassium acetate and alcohol. Ethyl acetate is very soluble in alcohol and ether. When it is perfectly dry it may be preserved indefinitely without decomposition, whilst, when it is moist, it gradually decomposes, regenerating alcohol and acetic acid.

Acetic ether is intermediate in danger between absolute alcohol and sulphuric ether. It is not quite so dangerous as ordinary ether. Hence it replaces the latter when the risk is too great. It burns with a yellowish flame and generation of acetic acid.

18. *Ethyl Nitrate.*—Chemical formula, $C_2H_5ONO_2 = C_2H_5NO_3$; it may be compared to nitric acid HNO_3, or potassium nitrate KNO_3, in which one atom of hydrogen (H) or potassium (K) is replaced by the organic radical, ethyl C_2H_5; molecular weight, 91·1; boiling-point, 87·2. It has an agreeable fruity odour. Its density is 1·123 at 15° C. When dropped on to a hot surface it sometimes explodes. It is soluble in water and mixes with all proportions in alcohol and ether.

It is prepared with precautions from its elements (nitric acid and alcohol) by distilling with the addition of a little urea. The crude distillate is shaken with water in a separating funnel (Fig. 28, Vol. I), the heavy oil dried with calcium chloride and distilled from a water-bath. It could be used in varnish-making as a solvent for Manila copal. But its use in this state is not to be recommended as it contains a large quantity of oxygen in unstable chemical equilibrium. Varnishes in which this substance has been used as a solvent are therefore liable to explode violently when suddenly heated. The substance itself explodes at 80° C. (176° F.).

19. *Ethyl Nitrite* (Nitrous Ether, when mixed with alcohol the sweet spirits of nitre of pharmacy).—Chemical formula, $C_2H_5NO_2$; molecular weight, 75·1; density, 0·900 at 15° C.; boiling-point, 17° C. Nitrous ether is generally prepared in the laboratory by slowly dropping concentrated sulphuric acid, 3 fluid oz., into a cold mixture of alcohol, 20 fluid oz., and 2 fluid oz. of concentrated sulphuric acid, then adding 4 oz. by weight of copper turnings and distilling from a water-bath. The crude distillate consists of a mixture of ethyl nitrite, unchanged alcohol, and its products of oxidation. To prepare the pure ether the distillate is shaken with water, the supernatant oil dried over calcium chloride and redistilled. Sweet spirits of nitre takes its name from its fruity odour. Ethyl nitrite is insoluble in water and is easily hydrolized by dilute alkalis or even by boiling water.

$$\underbrace{\underset{\substack{\text{Ethylic}\\ \text{Nitrite}\\ 75}}{C_2H_5{\cdot}NO_2} + \underset{\substack{\text{Potassium}\\ \text{Hydrate}\\ 56{\cdot}1}}{KOH}}_{131{\cdot}1} = \underbrace{\underset{\substack{\text{Ethylic}\\ \text{Hydrate}\\ \text{(Alcohol)}\\ 46}}{C_2H_5{\cdot}OH} + \underset{\substack{\text{Potassic}\\ \text{Nitrite}\\ 85{\cdot}1}}{KNO_2}}_{131{\cdot}1}$$

Nitrous ether is extremely volatile. At summer heat it is apt, on removal of the stopper of a bottle containing it, to evaporate very rapidly, and even to enter into spontaneous ebullition. It might possibly be used to increase the volatility of alcohol varnishes. But it explodes spontaneously at 90° C. (194° F.) during storage in contact with fat or organic matter and is a great source of danger in varnish works.

20. *Methyl Alcohol.*—Chemical formula, CH_3HO; molecular weight = 32; fluid, boiling-point, 66°-67° C.; melting-point, − 95° C.; density at 0° C., 0·789; flash-point, 32° F.; index of refraction: (1) (density of sample at 15° = 0·802), 1·3308 H^{α}; (2) (density of sample $\frac{t}{4}$ at 20° C., 0·7953) = 1·32789; molecular refraction, $p\frac{n-1}{d}$; determined, 13·19; calculated, 13·0; molecular refraction, $p\frac{n^2-1}{(n^2+2)d}$; determined, 8·16; calculated, 8·22.

The crude wood vinegar obtained in the distillation of wood contains about 1 per cent of wood spirit. It was in this liquor that methyl alcohol was first discovered by P. Taylor in 1812. The crude vinegar is again distilled, and the first tenth which passes over is collected apart. This is neutralized and repeatedly rectified with quick-lime, and the clear liquid, separated from the oil which floats on the surface and from the sediment, is treated with a small quantity of sulphuric acid which fixes ammonia and precipitates tarry matters, and is again distilled over quick-lime. The wood spirit of commerce is rarely pure. When mixed with water it generally turns milky, and an oily layer forms on the top consisting of different bodies insoluble in alcohol. The insoluble portion being separated, and the clear aqueous liquid distilled, methyl alcohol passes over first and is rectified over quick-lime. These processes are long and tedious, and only give imperfect results. When wood spirit is mixed with a fourth of its volume of olive oil, the latter combines with the impurities, and a comparatively pure methyl alcohol is obtained. A surer process is to distil the wood spirit with oxalic or citric acid so as to obtain a crystallizable ether (methyl oxalic ether). The latter is decomposed by distilling with water (after a previous purification by expression between folds of filter paper). The wood spirit thus obtained is rectified over quick-lime.

When pure, methyl alcohol is a colourless mobile liquid, possessing a spirituous odour. The empyreumatic odour of the wood spirit of commerce is due to impurities. Its density at 0° C. is 0·8142. It boils at 66·5° C. under the ordinary atmospheric pressure. However, its boiling-point varies between rather wide limits (60°-65°), according to the nature of the sides of the distilling vessel. Methyl alcohol is inflammable and burns with a non-luminous flame, and hence may be burnt in a spirit lamp. It mixes in all proportions with water, alcohol, and ether, and dissolves certain resins and fatty and volatile oils: its deportment in this respect being similar to ordinary ethylic alcohol, although its solvent action on gum resins is often different. Thus some resins are insoluble in ordinary alcohol, and also in wood spirit, but a mixture of certain proportions of these two dissolves the resin, but it often happens that an excess of either of the alcohols precipitates the resin from solution.

21. *Methyl Nitrate* (CH_3NO_3).—This ether of methyl alcohol is extensively used in the manufacture of methylaniline. It is prepared by introducing one part of nitrate of potash into a retort, and running on to it a mixture of two parts of sulphuric acid and one of methyl alcohol; the reaction occurs spontaneously without the aid of heat. A liquid distils which is led into a refrigerating condenser. The oily portion is afterwards washed with water, then rectified on the water-bath over a mixture of massicot (PbO) and chloride of calcium, collecting that which passes at 66° C. (150·4° F.). Methyl nitrate is colourless, with a faint ethereal odour; its density is 1·18 (36° Tw.) at 22° C. (71·8° F.). It boils at 66° C. (150·4° F.) and burns with a

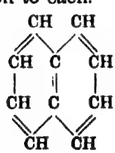
yellow flame. Very slightly soluble in water, it dissolves, in all proportions, in alcohol and in wood spirit. Heated to 100° C. (212° F.) with aniline, methyl nitrate is converted into methylaniline-nitrate, which, treated with caustic soda lye, yields methylaniline, which is distilled so as to render it fit for the manufacture of methyl-rosaniline colours. This is a far too dangerous solvent to use in varnish-making as suggested, as the liquid explodes on precussion or by a blow. Its vapour explodes at 356° F. (180° C.).

CHAPTER V.

SOLVENTS (*CONCLUDED*)—NAPHTHALENE, PETROLEUM SPIRIT, ETC.

22. *Naphthalene.*—Chemical formula, $C_{10}H_8$; molecular weight, 128·1; melting-point, 79°-80° C.; boiling-point, 218·2° C.; density, 1·145, 4° C.; index of refraction (at 98°, 4° C. D. = 0·962), 1·57456 (CH^a).

Naphthalene was discovered by Garden in 1820 and was examined a few years afterwards by Laurent. It is produced by the action of heat on numerous organic bodies, but only at very high temperatures, so that tars produced at a low temperature do not contain it at all. In the pure state naphthalene forms white crystalline masses or thin rhomboidal lamellæ. It melts at 79° C. The figures given for its boiling-point vary from 212° to 220° C. Naphthalene volatilizes much below its boiling-point, and consequently it can be distilled just as well in an atmosphere of steam as in that of the vapours of light coal-tar oil. That is the reason why it is present with the latter in crude coal-tar oils. But at the ordinary temperature it volatilizes slowly, exhaling a penetrating odour of coal-tar which adheres a long time to the clothes and keeps off moths and other insects. The researches of Erlenmeyer and Graebe have completely elucidated the composition of naphthalene, and it is now generally admitted to be formed by the amalgamation of benzene nuclei having two atoms of carbon common to each. (See benzene ring, p. 14.)



A large proportion of naphthalene may be obtained by simply allowing the heavy oil to stand till quite cold, separating the crude naphthalene (the purification of which is rather difficult) by filtration, centrifuging, or by pressure. The first pressing can be carried out in filter presses, the second in a hydraulic press. The purification may be carried a stage further by crystallizing the naphthalene from alcohol, and then subliming it, but this process is generally too costly. The crystallized naphthalene is generally washed with an acid or by an alkaline lye, but the acid treatment is preferable. According to Wohl, sulphuric acid of 45° B. should be used; however, this acid does not act in a sufficiently energetic manner, and it would be better to use acid of 60° B. at least. Sulphuric acid of 66° B. would act still

better; however, the latter at the temperature at which the reaction takes place dissolves a very appreciable amount of naphthalene which diminishes the yield but produces an excellent product. After washing with acid the naphthalene is washed with weak soda lye so as to eliminate all acid, after which it is distilled. The naphthalene is not yet always quite pure, however, because it reddens in the air after a greater or less length of time. To ascertain whether or not the naphthalene remains white in air and light, it is tested with sulphuric and nitric acid. Dissolved in slightly concentrated boiling sulphuric acid, naphthalene should only assume a weak violet or pale rose colour. To test with nitric acid, fuming nitric acid is poured into the bottom of a dessicator, and the samples of naphthalene are placed above it on watch glasses, and the whole covered. If they remain colourless for one and a half hours, or, better, for two hours, they are good, then the naphthalene purified chemically is distilled. It is more profitable to distil naphthalene than to sublime it, because larger quantities can be treated at a time, and afterwards, because it can be fractionated more exactly. It is essential, as in the case of tar, that the water in the vat around the worm should always be kept at 80° C. When naphthalene is distilled, there passes at the same time as the naphthalene a little water and traces of a light oil. When the thermometer in the vapour rises to 210° C. the still is "cut" and the receiver changed, and that which passes at 230° C. and on occasion up to 235° C. collected as pure naphthalene. Distillation is then stopped and the residue added to the heavy oil.

23. *Petroleum Spirit and its Congeners.*—The following products (Table X) are recovered from crude petroleum. The first five products are used as solvents. On the experimental and analytical scale in the laboratory the process is conducted as follows:—

TABLE X.—VARNISH SOLVENTS AND OTHER PRODUCTS RECOVERED FROM CRUDE PETROLEUM WITH THEIR DENSITY AND BOILING-POINTS.

	Density.	Boils between ° C.	
1. Petroleum ether (rhigolene)	0·65—0·66	40°—70°	Used as substitutes for turps, and to thin or adulterate it.
2. Gasolene	0·66—0·69	70°—90°	
3. Benzine cleaning spirit	0·69—0·70	90°—110°	
4. Ligroin	0·70—0·73	110°—120°	
5. Spirit for varnish	0·73—0·76	120°—170°	
6 ,, burning	0·76—0·80	170°—245°	
7. Burning oil	0·80—0·83	245°—310°	
8. Lubricating oil	0·83—0·87	310°—350°	
9. Paraffin, soft, melting-pt. 38-52° C.	0·87—0·88	350°—390°	
10. ,, hard, melting-pt. 52-56° C.	0·88—0·93	390°—430°	

Fractionation of Crude Petroleum Oil.—Wischin estimates the petroleum spirit, etc., in a crude oil as follows. The distillation is conducted in a cast-iron still (Fig. 4) capable of distilling two

litres of crude oil. Two thermometers are used, one t to indicate the temperature of the oil and the other t^1 the temperature of the vapour, and the oil is distilled into twenty equal fractions.

With a heavy mineral oil superheated steam can be used. A is the cast-iron still fitted with a wrought-iron still-head made tight by the screws S and asbestos packing. The two thermometers are screwed into the still, one of which dips into the oil and the bulb of the other is just opposite the vapour exit. When superheated steam is used it is led into the still through S. When the still is charged, cleaned, and closed, distillation is commenced and kept up so that the distillate issues as a uniform unbroken thin stream. Practice teaches how

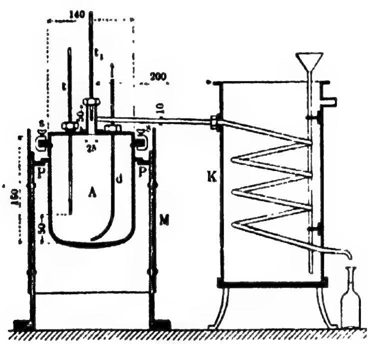


FIG. 4.—CAST-IRON STILL FOR FRACTIONALLY DISTILLING CRUDE PETROLEUM.
A, still; M, stand; P, support; S, screws; K, condenser.

to obtain a continuous flow instead of drops. During the distillation the temperature of the fluid and the vapour at each fraction is noted. The whole distillate is divided into twenty equal parts collected in 100 c.c. flasks.

		Specific Gravity.
Petroleum Ether	Cymogene	·590
	Rhigolene	·625 to ·631
	Gasolene	·635 to ·665

23*a*. *Gasolene.*—The crude naphtha from American or Russian petroleum, or that yielded by the distillation of Scotch bituminous shale, contains a very light, highly volatile, ethereal oil, with an unpleasant but highly characteristic smell, called "gasolene," distilling below 100° C., with a density varying from 0·6 to 0·7. Its principal use in varnish-making is as a quick evaporating vehicle or thinner for anti-fouling composition. *But its use is attended with great risk*—and varnishes or paints into which it enters should be stored and used *with most extreme caution*, as careless handling may bring about a terrific explosion. It should never be stored in the hold of a ship, and should only be applied to ships in open air in dry dock far removed from a flame, as the vapour, forming an explosive mixture with air, may run towards the flame and thus cause an explosion.

Composition.—Gasolene is a highly complex mixture of hydrocarbides, from which the following lower members of the series C_nH_{2n+2} have been isolated, viz. normal pentane C_5H_{12}, boiling at + 38° C., and isopentane C_5H_{12}, boiling at + 30° C., and normal hexane C_6H_{14}, boiling at + 71° C., an isomeric hexane as well as normal heptane, boiling at 98° C. It should be stored in drums placed in a watertight wooden receptacle underground or in underground tanks. When in use the drums should be immersed in cold water.

23*b*. *Petroleum Spirit, Mineral Turpentine, Mineral Naphtha, Shale Naphtha.*—These are not so volatile, and distil over after the gasolene. Their density is ·700 to ·760, and they boil between 120° and 170° C. American mineral naphtha may be differentiated from the Russian variety by its almost incomplete solubility in acetone, imparting thereto only a slightly yellowish or bluish tint. On the other hand, Russian mineral naphtha dissolves to a slight extent in that reagent. In applying this test the mineral naphtha ought to be neutral, which may be ascertained by treating it with cuprous oxide, which, in contact with acids, forms a copper soap soluble in the naphtha with a green coloration. Such naphthas have often a strong odour of noxious sulphuretted compounds, due perhaps to imperfect rectification; they may be deodorized by dehydrated green vitriol so as to smell more pleasant.

Petroleum spirit is a colourless liquid, with a powerful odour of petroleum and a strong blue fluorescence. It consists very largely of members of the paraffin series of hydrocarbons, with small quantities of naphthenes (American consists principally of paraffins, Russian of naphthenes), and members of the benzene series. According to Allen, cymogene consists largely of the gaseous hydrocarbon butane C_4H_{10}, rhigolene of pentane C_5H_{12}, and isopentane and gasolene of hexane C_6H_{14}, and isohexane. Petroleum ether consists principally of the hydrocarbons hexane C_6H_{14}, heptane C_7H_{16}, and octane C_8H_{18}, while burning oil is mostly composed of the hydrocarbons C_7H_{16} to $C_{12}H_{26}$. Dr. Sydney Young has separated and examined a number of paraffins and benzene hydrocarbons from petroleum spirit. Petroleum spirit is now largely used as a motive power in automobiles under the vague name of "petrol".

PART II.

OLEO-RESINOUS PINE PRODUCTS—TERPENES—CAMPHORS.

CHAPTER VI.

THE OLEO-RESINIFEROUS CONIFERS—CANADA BALSAM—OREGON BALSAM—STRASBURG TURPENTINE—VENICE TURPENTINE.

The Oleo-resiniferous Conifers.—The following is a list of the chief members of the pine family, the numerous species of which afford valuable timber, and resinous products.

(*a*) *European Oleo-resiniferous Pines*.—1. *Pinus Sylvestris.* The hardiest and most valuable of all the pines; its timber furnishes the red and yellow deal of the carpenters. Its resinous products—tar, pitch, and turpentine—are very valuable. It grows to the height of 80 or 90 feet; found on the mountains of Scotland and Northern Europe. It is abundant in Scandinavia, Siberia, and North America. Yields Russian turpentine.

2. *Larix Europea*—sometimes termed *Pinus Larix*—(the common larch). Next to the Scotch fir this is the most valuable of the tribe. Its timber is heavy, tough, and compact. Its average height is about 45 feet. It is a native of the mountains of middle Europe, widely diffused over Russia and Siberia, where it is the most common of all trees. It is extensively cultivated in England and Scotland *on barren and exposed land.* Yields Venice turpentine.

3. *Abies Excelsa* or *Pinus Picea* or *Pinus Abies* (sometimes called Norway spruce). This noble tree rises in a straight stem from 150 to 200 feet in height. Its timber is known as the white fir or deal. Grows in the countries of Northern Europe, and is found throughout Siberia to 70° North latitude. Yields Burgundy pitch.

4. *Pinus Pinea* (the stone pine). The timber of this tree is used in shipbuilding. A native of Southern Europe and the Levant.

5. *Pinus Pinaster* or *Pinus Maritima* (the cluster pine). This noble species affords a great quantity of resin and tar, but its timber is light, soft, and coarse. Inhabits the barren plains of France and Southern Europe, especially in coast districts, to prevent encroachment of sand dunes. Crooked stem. Yields French turpentine.

6. *Pinus Corsica* or *Pinus Laricio.* This tree grows very fast and yields excellent timber. Grows in the mountains of Corsica, Spain, Greece, and Turkey. Yields Austrian turpentine.

7. *Pinus Canariensis* (Canary pine). Timber resinous and durable. It is peculiar to the mountainous districts of the Canary Islands, and principally to Teneriffe.

8. *Abies Pectinata* (the silver fir) yields Strasburg turpentine.

(*b*) *Asiatic Oleo-resiniferous Pines* (pp. 63-6).—Asia also furnishes various species of pines, e.g. P. Halepensis (the Aleppo Pine), P. Cembra; P. Sibirica, P. Neoza, P. Deodara, P. Excelsa, P. Longifolia, P. Merkusii, P. Khasya, P. Gerardiana (Wall), P. Orientalis, P. Sinensis, etc., etc.

(*c*) *North American Oleo-resiniferous Pines.*—*Picea Balsamea* attains to the height of 50 feet, and *yields the resin Canada balsam.* It is found in the cold regions about Great Slave Lake, and the Alleghany Mountains. The tree is valueless for timber, being cultivated for the turpentine which it yields. The resin collects in small bags on the exterior surface of the bark, and is ready for collection during June, July, and August, each tree furnishing about 1 lb. of resin (see pp. 45-9).

Abies Alba yields timber of a large size, but not so resinous as the Norway spruce. Its bark is used for tanning. Abundant in Nova Scotia and Canada.

Abies Rubea attains the height of 30 feet. Grows in Nôva Scotia, Newfoundland, and the shores of the Hudson Bay.

Abies Canadensis, a noble tree of slow growth, attaining a height of 80 feet. Its timber is not good, but its bark is valuable for tanning. Extends from Alleghany Mountains to lat. 50° N. It is very abundant in Nova Scotia, New Brunswick, near Quebec, and in Vermont. Yields Canada balsam (pp. 45-9) (Syn. Hemlock Spruce).

Pinus Resinosa Sol. : *Pinus Rubra Michaux* [The Douglas Spruce] (pitch pine or red pine of the Canadians), remarkable for its great height (80 to 100 feet), and its smooth red bark, and yields a great quantity of fragrant resin. Found in Canada and the Northern regions of America. It grows in close forests. Yields Oregon balsam.

Pinus Strobus (white or Weymouth pine). This is the largest species to the East of the Rocky Mountains, being found to attain to a height of 200 feet. Timber valuable for ships' masts. Grows in Canada and the United States, about Lake Champlain, on Fundy Bay, etc.

Pinus Rigida (the pitch pine). Timber cross-grained, and of inferior quality, yielding abundance of tar. Found in the greater part of the United States on poor soils. The term pitch pine is applied in Britain to wood of P. Palustris (pp. 60 *et seq.*), *v. infra.*

Pinus Ponderosa (bull pine). Timber heavy and durable, but coarse. Found in North-West America. The essential oil is said to contain heptane! (Thorpe, Schorlemmer), (see p. 68).

Pinus Australis : *Pinus Palustris* (longleaf pine). Timber light, clean, and durable; used for masts of ships, and yields abundance of tar. Found in the middle countries of North America. Pine wastes North Carolina to Texas. Exploited for oleo-resin; the pitch pine of British carpenters (see pp. 60-63).

Pinus Taeda (the loblolly pine), (sometimes called the frankincense pine), attains a height of 80 feet. Timber soft and not durable. The tree yields abundance of fragrant turpentine. Grows in the

barrens of Florida and Virginia. Contributes its contingent to American turpentine. Confused with P. Palustris.

DETAILED DESCRIPTION OF INDIVIDUAL OLEO-RESINS.

1. *Canada "Balsam" : Botanical Source:—Abies Canadensis*, L. Miller, and allied species. Fluckiger, Wiesner, Sayre, and others give only *Abies balsamea*, Marchall (*Pinus balsamea*, L.), or only *A. Canadense*, Mich, as the sole producing tree. *Pinus Fraserii*, Pursh, is, however, recognized as a source of Canada balsam. But in any case all the species are closely allied. *Geographical Origin.*—The oleo-resin is collected in the Lorenz Mountains of the Province of Quebec in Canada. The *Pinus balsamea* frequents bleak mountainous tracts, is about 35 feet in height with a diameter of 8 inches, is worthless for timber, and is only valued for its oleo-resin. It would also appear to be collected in the northern part of the Alleghany Mountains from *Pinus* (*Abies*) *Fraserii* and *Abies Canadensis*.—*Physiology and Morphology.*—The secretion vessels of the balsam fir, like those of *Abies pectinata*, the silver fir (pp. 49 *et seq.*), etc., are located in the bark; they are long and segregate into a tumour-shaped vesicle but not by lysigenous swelling. That of the young branches is not yet visible.

Method of Collecting the Oleo-Resin.—This is a very trying task, and is only undertaken in the Province of Quebec by the very poor, viz. the Red Indians. In the month of June the "balsam" collectors with their families betake themselves to the mountains, where they encamp, with little baggage, for about two months in the open air. The women remain in the camp and see to the filtering or straining of the "balsam". In Lower Canada the "balsam" is collected by means of small tin cans, fitted with a spout with a sharp lip, which they drive into the tree through the bottom of the vesicle. The sharp spout not only fixes the can but conveys the balsam which drains into it into the can. The father with his young children taps the vesicles in the tree which he knows are full of balsam in the manner indicated. When the can is full it is emptied. A full-grown tree rich in oleo-resin only yields 8 oz. of oleo-resin. A man with the help of two children can collect a gallon daily, but by himself alone only half a gallon. The collector cannot work in rainy weather as water renders the balsam milky and unsaleable. The women carry the balsam in canisters of five gallons each into the village, where they sell the balsam, and with the money buy food to bring back with them. At the end of August, when the snow begins to fall on the mountains, and the weather is so cold that the oleo-resin ceases to flow, the collectors return to the village. A tree can be tapped for two years, but it must then be let rest for two to three years, but the after-yield is always smaller. Montreal and Quebec export together about 20 tons yearly.

General Appearance and Properties.—The oleo-resin when fresh is a viscous, straw-coloured fluid with a faint greenish play of colour,

and a feeble fluorescence. The aroma is characteristic and strong but not unpleasant, and the taste is bitter. Its density is 0·998 at 58° F. It is completely soluble in ether, amyl alcohol, benzol, chloroform, spirits of turpentine, carbon tetrachloride, carbon disulphide, toluol; in ethylic alcohol, methylic alcohol, acetone, acetic acid, acetic ether, and petroleum ether it only dissolves partially, leaving a white residue. In the air a film of Canada balsam dries to a clear transparent varnish which in nowise exhibits a crystalline appearance.

Chemical Composition of Canada Balsam.—Canada balsam was first analysed in 1825 by Bonastre and later on by Fluckiger. Their results are given in parallel columns in the following table:—

TABLE XI.—SHOWING THE CHEMICAL COMPOSITION OF CANADA BALSAM ACCORDING TO BONASTRE (I.) AND FLUCKIGER (II.).

	I. Per cent.	II. Per cent.
Essential oil	18·6	24·0
Resin soluble in alcohol	40·0[1]	59·8
Resin difficultly soluble	33·4	16·2[2]
Elastic resin	4·0	—
Extractive and salts	4·0	—
	100·0	100·0

The index of refraction of Canada balsam is 1·532. The essential oil of Canada balsam is levo-rotatory − 6·7° to − 7·2°. The balsam itself is dextro-rotatory + 2°. The bitter principle dissolves in water when the balsam is warmed therewith. It gives precipitates with iron chloride, lead acetate, and tannic acid, but is not, however, a glykoside.

Physical Properties of Canada Balsam.—This oleo-resin is differentiated from all other turpentine oleo-resins by its great capacity for refracting light, which is so great that a potato starch granule embedded in a layer of the balsam remains clearly visible, whilst in the oleo-resin from any other conifer it is not clearly seen or almost completely disappears.

Six samples of this oleo-resin, according to the essential oil correspondent of "The Oil and Colour Trades Journal," yielded the following figures:—

TABLE XII.—ACID AND SAPONIFICATION VALUES OF CANADA BALSAM.

	Acid Value[3]	Saponification Value.[4]		Acid Value.	Saponification Value.
1	106·4	116·2	4	97·5	112·1
2	98·0	107·8	5	86·8	105·3
3	98·0	112·0	6	87·5	105·3

[1] Dieterich gives this figure as 46 per cent. Needless to say, his figures total to 106. Tschirsch gives the same figure as Dieterich.

[2] Insoluble in alcohol but readily soluble in ether. Fluckiger found both acids reddened litmus, but could obtain no crystalline substance from either.

[3] Number of milligrammes of KHO to saponify free acid in 1 gramme of resin.

[4] Number of milligrammes of KHO to completely saponify 1 gramme of resin.

Kremel found the acid value by the direct method, one gramme in alcohol titrated with $\frac{N}{10}$ potash = 83·0 and 81·3 F. Dietz found the following figures :—

TABLE XIII.—ACID ESTER AND SAPONIFICATION VALUE OF CANADA BALSAM.

	I.	II.	III.
Acid value, direct	84·89	85·93	84·40
Ester value	4·54	9·83	9·00
Saponification value	89·43	95·76	93·40

E. Dieterich found acid value, direct, 84·0-86·8.

Tschirsch resolved Canada balsam by the methods described in the sequel and the data thereby obtained into

TABLE XIV.—SHOWING THE COMPOSITION OF CANADA BALSAM (ACCORDING TO TSCHIRSCH).

	Per cent.
Canadinic acid	13-14
Canadolic acid	0·3
α-Canadinolic acid, β-Canadinolic acid	48-50
Essential oil	23-24
Canado resene	7·0
Mixture of resene and essential oil	5·0

Tschirsch gives the following constants : Acid value, direct, 82·18-86·10 ; indirect, 84·56-85·09. Saponification value, cold (twenty-four hours), 94·24 ; (forty-eight hours), 93·24 ; (seventy-two hours), 93·35 ; (eight days), 93·36. Saponification value, hot (one hour), 101·24 ; (two hours), 197·7 ; (four hours), 197·48. On *dry* distillation succinic acid, of melting-point 184·5° C., was obtained in addition to formic and acetic acids. Ammonium carbonate extracted 13-14 per cent which could not be crystallized from any solvent, but from which lead acetate precipitated an acid—*Canadinic* acid—soluble in all solvents with the exception of water and petroleum ether ; melting-point, 135°-136° C. Its solution reacts acid and has no action on polarized light. On analysis it gave: Found mean of three analyses: C = 77·33 ; H = 11·95. Calculated for $C_{19}H_{34}O_2$: C = 77·55 ; H = 11·56. For $C_{20}H_{38}O_2$: C = 77·42 ; H = 12·26. Acid value, direct, 191·8. Saponification value, cold, 191·7 ; hot, 191·8. There is thus no difference between the acid value and the saponification value. Canadinic acid behaves like larocinolic acid (pp. 56-7), abietolic acid, and abietinic acid (pp. 50-1). Titration shows canadinic acid to be monobasic ; 13·5 per cent K was required to form the potassium salt. $C_{19}H_{34}O_2$ requires for formation of the potassium salt $C_{19}H_{33}KO_2$, 13·26 K. One per cent soda extracted 50 per cent of an acid mixture which gave a saponification value and which was separated into two parts by lead acetate. Without lead acetate an amorphous acid falls out ; the crystalline *canadolic* acid melting at 143-145° C., falls after the greater part of the uncrystallizable acid has settled out. It forms crystals like abietinic acid soluble in all solvents and in petroleum

ether. Analysis gave: Found mean of three analyses: C = 79·22; H = 9·74. Calculated for $C_{19}H_{28}O_2$: C = 79·16; H = 9·72. For $C_{20}H_{30}O_2$: C = 79·47; H = 9·93. A molecular weight estimation gave mean of six analyses = 299. Calculated for $C_{19}H_{28}O_2$ = 288. Acid value, direct, 191·8. Saponification value, cold, 247·8; hot, 328·3.

Canadolic Acid, in contrast with canadinic acid and the amorphous acids about to be mentioned, α and β canadinolic acid, yields a saponification value, and here it is to be noted that in one and the same secretion are present an acid which gives a saponification value and with other acids which do not do so. Canadolic acid is a monobasic acid. By direct titration it took 13·36 to form the potassium salt. $C_{19}H_{28}O_2$ requires for the formation of the mono-potassic salt $C_{19}H_{27}KO_2$, 13·54 per cent K. Canadolic acid in the crystalline form very much resembles abietinic acid (p. 50). Its empirical formula is the same. It is differentiated from it, however, by its behaviour with lead acetate; it is not precipitated. It differs also in the melting-point. Canadolic acid is accompanied by two amorphous acids, one of which is precipitated by lead acetate, the other not—α and β canadinolic acid. They are present to the extent of 40-50 per cent, or one-half in the oleo-resin.

α-Canadinolic Acid, precipitated by lead acetate, soluble in all solvents, also in water and petroleum ether; melting-point, 95° C.; intumesces at 89° C.; optically inactive. Analysis (mean of three): C = 78·55; H = 10·59. Calculated for $C_{19}H_{30}O_2$: C = 78·62; H = 10·34. Salt formation value: Found percentage, K = 13·92. Calculated for $C_{19}H_{27}KO_2$, 13·4° K. Acid value, 199·8. Saponification value, hot (twenty-four hours), 200·1; (one hour), 200·7.

β-Canadinolic Acid, not precipitated by lead acetate, soluble in all solvents, also in water and in petroleum ether; melting-point, 95° C.; intumesces at 90° C.; optically inactive. Analysis (mean of three): C = 78·64 ; H = 10·59. Salt formation value: Found percentage, K = 13·77. Acid value, 197·7. Cold saponification value (twenty-four hours), 199·1. Hot saponification value after one hour, 198·8. Both acids are monobasic and give no saponification value. They are isomers. The resin acids being removed by ammonium carbonate, and soda and potash having extracted nothing further, the residue was distilled with water to free it from essential oil. The remaining resinous body, 7 per cent of the whole, resisted the action of alkalis both hot and cold. It is therefore a resene. It was accordingly purified by precipitating its ethereal solution by alcohol. It follows that it is insoluble in alcohol. Its solubility is interesting. It dissolves easily in ether, with more difficulty in amyl alcohol, benzene, chloroform, spirits of turpentine, carbon disulphide; incompletely in petroleum ether; almost insoluble in ethyl alcohol, methyl alcohol, acetone, acetic acid, acetic ether, and water. The substance was termed *canado resene*. Mean of three analyses: C = 81·86; H = 12·87. Calculated for $C_{21}H_{40}$: C = 81·82 per cent; H = 12·99 per

cent. Here it is to be remarked, as in the case of other coniferous resins, on shaking the ethereal solution with soda solution a substance settles out on the line of separation of the two fluids. It is a mixture of canado-resene with oil. If the latter be removed by distillation with steam, and the residue purified as above, pure canado-resene is obtained, likewise giving on analysis C = 81·80 per cent; H = 12·91 per cent. The mixture amounts to 5 per cent of the balsam. About half the amount of the resene present is thus removed by shaking. Canada balsam likewise contains 23-24 per cent of an essential oil, the greater part of which passes over between 160° and 167° C.

Uses.—Canada balsam is used to cement lenses, Nicol's prisms, etc., for polarimetric and refractometric work, also in the mounting of microscopic objects. It is used in the preparation of transparent paper for imitation glass printing so as to render it transparent. For this purpose the paper is dipped into a solution of the balsam in turpentine oil and after drying it is given another dip.

Benzene is most esteemed as a solvent. When it dries from its solution in the latter or in chloroform it leaves a perfectly transparent faintly yellow and beautifully lustrous film.

2. *Oregon Balsam from Abies Amabilis.*—A sample of Oregon balsam examined by Evans: Acid value, 80; saponification value, 86; and the oil obtained by distillation yielded the following results on examination:—

	(1)	(2)
Specific gravity	·867	·865
Optical rotation	– 36	– 37° 24′
Acid value of rosin	152·6	153

The utmost confusion has hitherto existed with regard to Oregon balsam, three kinds, *Abies concolar*, *amabilis*, and *nobilis*, furnishing a balsam similar to that from *Abies balsamea*. Rabak ("Pharm. Review"), in an attempt to clear up the matter, gives a description of the oleo-resin from *Abies amabilis*, coming from the valley of the Oregon and of the oil distilled therefrom. He obtained 700 grms. of the oleo-resin, which is a pale yellow liquid, having an odour resembling that of limonene. Its specific gravity at 22° C. is 0·969, and its 10 per cent solutions in alcohol and ether are optically inactive. On distillation it yields 40·3 per cent essential oil, which, while paler in colour, has the same odour as the oleo-resin. The specific gravity of the oil at 22° is 0·852, and its optical rotation 14° 24′. The oil has been fractionally distilled, and it is concluded that it consists chiefly of pinene with a little limonene.

3. *Strasburg Turpentine* (*Terebintha Argentoratensis*).—The oleo-resinous products of the silver fir are very valuable. The substance called Strasburg turpentine, from a large forest of silver[1] fir trees near Strasburg, is collected from small tumours or blisters under the cuticle of the bark; the tapping therefore consists in simply piercing

[1] *Abies pectinata.*

the tumours, which is done by a white-iron cylinder drawn out obliquely to a point so as to simultaneously puncture the pockets and collect the resin. Strasburg turpentine having now almost disappeared from the market, analytical data are lacking. The oleo-resin of the white pine agrees perfectly well with Canada balsam except as regards solubility, the former mixing in all proportions with glacial acetic acid, acetone, absolute alcohol to a clear solution. The odour of the white pine resin is also more agreeable, being known in France as *terebenthine au citron.* The taste is not sharp like that of Canada balsam and is less bitter. No fluorescence is perceptible.

Weigel and Tschirsch examined Strasburg turpentine. The sample was amber-yellow-brownish, of the consistency of thick syrup; the smell was between lemon and balm. It had a sharp taste and the after-taste was bitter. It dried in a thin layer in the air to a transparent pale varnish. Density = 1·12. It gave no methyl value and dissolved in usual solvents, but only partially in ethyl and methyl alcohol, acetone, and petroleum ether. Its solution in ethyl alcohol reacts strongly acid. Acid value: direct, 78·4-84; indirect, 81·2-86·8; saponification value: cold, 140-145; hot, 151·2-154. Dry distillation yielded succinic acid; melting-point, 184. Saponification yielded none. The succinic acid is therefore a decomposition product. Water extracts the bitter principle. Ammonium carbonate extracts 8-10 per cent of the balsam. Fifteen extractions were required for 500 grammes of turpentine. The separated resin had not to be separated from any entrained matter. It formed a white powder melting at 114°-115° and optically inactive. This acid, *abietinic* acid, yielded on analysis: Mean of three analyses: C = 79·94; H = 9·25. Calculated for $C_{14}H_{20}O_2$: C = 75·00; H = 9·62. Acid value, 176·4; saponification value: cold, 238; hot, 257·6. The acid is monobasic and forms a monopotassium salt when boiled with aqueous potash. The potash content calculated from titration gave 15·21. The formula $C_{13}H_{19}KO_2$ requires a content of 15·83 K. Extraction with soda solution: twenty-three extractions yielded 48-52 of a resin acid mixture, which on crystallization from methyl-ethyl alcohol gave a small amount of a crystalline acid (2 per cent). This *abietolic* acid crystallized like abietinic acid in needles, mostly in plates which not seldom reach 5 mm. in length. The crystals begin to melt at 136° C., but melt for the first time at 152°-153° C. The solution is inactive. Mean of four analyses found: C = 79·79; H = 9·59. Calculated for $C_{20}H_{28}O_2$: C = 80; H = 9·33. Molecular weight: Mean of five analyses, 283. Calculated for $C_{20}H_{28}O_2$, 300. The potassium salt by direct titration gave 11·62 per cent K. $C_{20}H_{27}KO_2$ requires 20·74 per cent K. The greater part of the resin acid extracted by soda is amorphous. The acid mixture can be separated by lead acetate. a-abietinolic acid is precipitated, β-abietinolic acid is not.

a-Abietinolic Acid.—Melting-point, 95°-96° C. Found mean of two analyses: C = 77·34; H = 9·55. Acid value, direct, 218·4; saponi-

fication value: cold, 235·2; hot, 235·6. Found, K = 13·2. Calculated for $C_{19}H_{23}KO_{2}$, K = 13·64.

β-Abietinolic Acid.—Melting-point, 93°-94° C. Found mean of three analyses: C = 77·15; H = 9·44. Acid value, direct, 217; saponification value: cold, 229·6; hot, 266. Found, K = 13·1. Calculated for $C_{16}H_{23}KO_{2}$, K = 13·64. Both acids are thus monobasic. The abietoresen is obtained by precipitating the ethereal solution with alcohol in which it is insoluble. Purified it melts at 168-169° C. It dissolves in usual resin solvents, on heating in acetic ether, slightly in petroleum ether and hot glacial acetic acid, and is insoluble in ethyl and methyl alcohol and acetone. Analysis gave mean of three analyses: C = 83·11; H = 11·15. Calculated for $C_{19}H_{30}O$: C = 83·21; H = 10·95. The resene is present to the extent of 12-16 per cent; essential oil is present in Strasburg turpentine to about 30 per cent. It passes over in greater part between 148°-165° C. It has a pleasant smell. The balsam distilled with lime emits an odour of roses and orange flowers. (See Table XV, p. 74, under Silver Fir.)

4. *Venice Turpentine—History.*—This oleo-resin was known to Pliny, who describes it as follows: "Plusculum huic erumpit liquoris melleo colore atque lentiore nunquam durascentis" (This resin, which is honey-coloured, issues slowly from the larch-tree, but never becomes dry). Again, Dioscorides states: "There are liquid resins also from the pine and pitch-tree. These are brought from France and Etruria. They vary in colour, as some are like oil, others white, and some like honey, as the larch." Moreover, the *atramentum* of Pliny, "which" (he states) "was applied so thinly over the picture when finished that it brought out the colours in all their brilliancy and preserved them from dust and dirt". "Quod absoluta opera atramento illinebat ita tenui ut idipsum repercussa claritatis colorum excitaret custodietque a pulvere et sordibus."

Origin.—It is obtained from bore-holes made for the purpose in the common larch—*Pinus larix* (L.), *Larix decidua* (Mill.), *Larix Europea* (De Candolle)—which is grown for resin-producing purposes in the Tyrol, Piedmont, and in France in the environs of Briançon.

The larch-tree has been acclimatized in Scotland and in Norway, being grown in those countries more especially for telegraph poles, but in neither country has it been exploited for its oleo-resin. It does not always thrive well in Scotland, being subject to a peculiar disease called the larch disease, which has quite a special literature of its own. Possibly this disease is induced by the extreme poverty of the soil in which it is planted, more especially on a shallow soil resting on moorband pan, into which the roots of the larch cannot penetrate. A severe storm, moreover, easily fells the trees. Some years ago a good portion of a forest was swept to the ground in a wholesale manner just above the Pass of Killiecrankie. The fifth Duke of Athole in his memoranda regarding his Dunkeld and Athole larch plantations brought out in a striking manner the immense increase in

the value of land that may be effected by planting. It appears that the land on which his plantations were made was not originally worth more than a rental of 9d. to 1s. per acre, but such was the effect of the amelioration of climate and the improvement of the soil produced by the foliage, that at the end of thirty years, when the last thinnings were removed, cattle were kept on the land both summer and winter, and showed the *pasture alone* under the trees to be worth 10s. per acre rental. Encouraged by such results the Duke planted, during the latter years of his life, 6500 acres with larch only, which he confidently calculated would in seventy years from the time of planting be worth £1000 per acre, even at the low price of 1s. per cubic foot, or less than one-half the price at which he then sold, and that the timber would be fit for building ships of the larger class. The expense of planting and fencing did not in any case exceed £2 per acre, and the greater part was executed at 10s. per acre. But iron ships have since the Duke's time replaced wooden ones, and the drain on Scottish timber for shipbuilding has ceased, though not until it had deforested Strathspey of its true native Highland Scots pine forests, and the denudation of the catchment basin of the Spey was the sure cause of the disastrous Moray floods of 1829, so well depicted by Sir Thomas Dick Lauder. In how far the Duke's estimate of £1000 per acre after seventy years is justified will readily appear from the photograph of two trimmed but unbarked trees, evidently 100 years old, felled in 1909 in the forests in the neighbourhood of Cawdor Castle and awaiting shipment on Nairn Harbour. The trees were intended for mast-making. The photograph was specially taken for the second English edition of this treatise. According to a recent Kew Bulletin the cost of planting is now (1910) much higher, but it is interesting to know that the Lochiel forest of highly resinous true Scots pines some miles in extent, is still to the fore though over 200 years old.

According to Prof. Voerl of Venice the method of tapping the larch and collecting Venice turpentine in the Austrian Tyrol is still (1900) the same as described by Hugo Von Mohl in 1859. The tapping is based on the fact that the oleo-resin tends to accumulate towards the centre of the stem and that it often fills the cavities made in the trunk by frost. To collect the oleo-resin, a bore-hole 1 in. to 1½ in. wide and sloping downwards, outwards, or horizontal, is drilled by means of an auger, early in the year, in mature trees 40 in. in girth. The hole penetrates as far as the axis and is about 12 in. from the ground. This channel is carefully cleaned, and corked up hermetically by a dry larch spigot, which prevents loss by evaporation. The collector bores from 50 to 100 trees in a day. In autumn the cavities are emptied by means of an auger. The same bore-hole can be used over again; it is then on the second or third emptying widened to a maximum of 1·6 in. The yield is, on an average, nearly half a pound of oleo-resin per tree. This is a poor yield, but the working entails little labour, and yields a product

of exceptional purity, which commands a price three times higher than the pine oleo-resin. The trunk is but little injured and the same cavity yields resin for thirty years (twenty years). The bore-hole is again hermetically sealed during the winter. From the Tyrol markets the oleo-resin almost exclusively goes south through Verona to the great market emporiums of Venice. In the second Venetian turpentine centre, lying near Briançon in Dauphiné, and in Piedmont, near Pinerolo, south-east of Turin in the Maritime Alps, in order to obtain it holes are pierced with augers as usual in the Austrian Tyrol, but into these holes wooden tubes are inserted, through which the oleo-resin flows into little buckets sus-

FIG. 5.—Scottish grown larch trees showing over 100 rings of annual growth felled near Cawdor, Nairn, 1910.

pended at the other end to receive it. The season for collecting it lasts from May to October. According to Mohl, and also Wesseley, the bore-hole in the Italian Tyrol is mostly open and is not closed till the oleo-resin ceases to flow, but in fourteen days the outflow of oleo-resin is again resumed. It is perfectly clear, and needs no further preparation than straining through a coarse haircloth to free it from impurities. Venice Turpentine derives its name from the city of Venice, from which it was formerly exclusively exported. Venice turpentine resembles golden syrup or honey in colour and consistency. Pliny has well remarked that it never dries. It varies in colour from bright to greenish-yellow. It is naturally cloudy and dull, but freed from contained water and air-bells it is bright

and clear. In thin layers it quickly clarifies but takes longer in bulk. It has a faint fluorescence (Andes, Fluckiger). The rosin from larch is dextro-rotatory, the essential oil levo-rotatory. Its smell recalls lemon and nutmeg. The invariably bitter taste is due to pinipicrine, a glycoside found in conifers by Kawalir. Venice turpentine is *soluble* in 90 per cent alcohol, acetic ether, chloroform, benzol, and spirits of turpentine (E. Dieterich); also in acetone, ether, glacial acetic acid, methylic and amylic alcohols (Erban and Schmidt); almost entirely soluble in petroleum ether, ether, and carbon disulphide (Dieterich). Venice turpentine oleo-resin does not like other turpentine oleo-resins separate into two layers in course of time, and it does not eventually harden on the surface, nor become crumbly when kept for a long time in a cold place. It shows no crystals when viewed under the microscope. It becomes fluid at a low heat, and then runs easily. Its composition is given in Table XV, but its percentage of essential oil is said to vary from 15 to 25 per cent. K. Dieterich got the following "constants": Acid value, 66·92-68·85; ester value, 46·27-54·94; saponification value, 114·56-127·71. Beckhurst and Brook's figures are: Density, 1·094-1·190; acid value, 76-101; ester value, 0·9; saponification value, 81-101. The acetyl values (K. Dieterich) are: Acetyl acid values, 69·87-72·19; acetyl ester values, 109·08-118·67; acetyl saponification values, 178·95-190·86; methoxyl value, 0. Tschirsch says the variations in the saponification values are due to the greater or less capacity of the resin acids for combining with alkali and that the oleo-resin contains no ester.

Adulteration.—There are numerous concoctions on the market sold as Venice turpentine which do not contain a particle of it—mixtures of rosin, rosin oil, and turpentine, none of which are completely soluble in 90 per cent alcohol but form emulsions therewith and separate out on standing (characteristic of rosin oil). The real article is often sophisticated with common turpentine, which may be detected by heating gently to drive off the volatile oil and then moistening the residue with alcohol; if the residue treated thus has a crystalline appearance common turpentine is present. Smell is a useful guide, together with the inflammability and solubility in alcohol. To detect ordinary turpentine oleo-resin in larch turpentine oleo-resin the Hübl saponification recommended by some is unsuitable, because the acid and ester values thereby obtained vary considerably, both in ordinary and in larch turpentine oleo-resins.

If a little common turpentine oleo-resin be suffused with dilute ammonia of 0·96 gravity a milky emulsion is produced, but larch turpentine remains clear. On stirring the latter it does not mix but behaves as an oily mass in the aqueous liquid, without apparent change, but is gradually transformed to a semi-solid, colourless, opaque mass, the liquid being but slightly turbid. But common turpentine oleo-resin immediately diffuses through the ammoniacal liquor, and forms an emulsion which soon sets to a jelly, especially when the pro-

portions are 1 part of turpentine oleo-resin to 5 of ammonia. Larch turpentine oleo-resin, mixed with 5 per cent of ordinary turpentine oleo-resin, diffuses very readily in ammonia, the mixture settling in about five minutes, and clarifying when placed in hot water. A mixture containing 30 per cent of ordinary turpentine oleo-resin is also easily diffusable, solidifies in about ten minutes, and clarifies in the water-bath, but any smaller proportion than 20 per cent of common turpentine oleo-resin can only be detected with certainty when a genuine sample is available for comparison. The presence of not less than 30 per cent of ordinary turpentine oleo-resin may be detected by 80 per cent alcohol. If 1 part of the turpentine oleo-resin be mixed with 30 of this alcohol and shaken up a clear solution is formed if the sample be pure larch turpentine oleo-resin, whereas over one-half the amount of any ordinary turpentine oleo-resin will separate out after a short time. The test is not infallible, but may be resorted to in doubtful cases. The importance of the acid and saponification value in indicating quality is evident, as both these "constants" are far higher in ordinary than in Venice turpentine oleo-resin, so that the presence of large admixtures of the former can be detected in this way. The acetyl value for ordinary turpentine oleo-resin is also far greater than for larch turpentine oleo-resin. But the best test of any (one which all authorities, curiously enough, omit) would be obtained by examining the action of the essential oil produced by the wet steam distillation of the oleo-resin on a ray of polarized light. This affords a more sure guide to sophistication in regard to a factor more likely to be overlooked by sophisticators of the ordinary calibre. The refractive index of both the oleo-resin and its essential oil ought also to provide additional aids to the identification of adulterants. In regard to the concoctions previously referred to in which Venice turpentine is conspicuous by its complete absence, Schaal prepares a turpentine of this nature by distilling pine resins *in vacuo* at 270° C. and subsequent distillation with oil of turpentine under reduced pressure. E. Dieterich gives for one of these "artificial" Venice turpentines: Acid value, 98·79; ester value, 0·88; saponification value, 97·66. Von Itallie says the acid and saponification value of these products are almost alike, but genuine Venice turpentines have the acid value 70 and the saponification value 120. He gives the following figures for two solutions of rosin in rosin oil (apparently a sort of white ships' varnish!): Acid value, 97-99·5: saponification value, 108·0-109·3.

Venetian turpentine was first examined by Berzelius and Unverdorben. Unverdorben found therein two ethereal oils, from the heaviest of which a little succinic acid distilled (both by distillation of the oleo-resin over water) much pinic acid, a neutral resin soluble in petroleum oil, and a little neutral resin insoluble therein as well as a bitter extractive matter but no silvic acid. Lecanu and Serbat found succinic acid amongst the dry distillation products. Maly examined the resin dried on the stems of the larch-trees as well as the overflow resin (p. 58). He found in it a crystalline substance

which he recognized as abietinic acid (p. 50). Ducommun asserts that the oleo-resin contains no crystalline body. He remarks: "There is a record by Caillot of a crystalline body, laricin, contained therein, but all chemists, such as Fluckiger, who have examined Venice turpentine agree clearly on the point that it contains no crystalline acid. The ethereal oil of Venice turpentine contains pinene." Tschirsch examined, on the one hand, a market sample of Venice turpentine from genuine sources (Caesar and Loretz C. Haaf), on the other hand, a sample obtained direct from Pergine (Farmacia Crescini). The balsam was clear with a feeble fluorescence and dried to a clear varnish. Its density was 1·185, methoxyl value nil. It deviated the plane of polarization to the right, the ethereal oil to the left. Acid value: direct, 68·6-71·4; indirect, 70-72·8; saponification value: cold, 128·8-134·4; hot, 137·2-145·6. By long-continued dry distillation of 75 grammes of the oleo-resin 0·1 gramme of succinic acid was obtained, identified by its reactions and melting-point, 182°-183° C. Boiling water in large quantities extracted a bitter principle from the oleo-resin but no glucose. Whether the bitter principle is identical with that found in the needles of *Pinus sylvestris* by Kawalir in 1883 is doubtful (p. 54). By extraction with ammonium carbonate a small amount of a phlobaphene was obtained. A 1 per cent soda solution extracted 60 per cent of the weight of the oleo-resin. The crude acid separated by hydrochloric acid was dissolved in ethyl-methyl alcohol for crystallization to occur, the greater part of which when recrystallized intumesced between 135°-136 C., began to melt at 140° C., and fused at 147°-148° C. It dissolves completely in the usual resin solvents and completely in petroleum ether. The inactive laricinolic acid reacted acid. Market sample, mean of three analyses: C = 79·51; H 9·63. Pergine sample, one analysis: C = 79·53; H = 9·74. Calculated for $C_{20}H_{30}O_2$: C = 79·47; H = 9·94. For $C_{19}H_{28}O_2$: C = 79·16; H = 9·73. Molecular weight estimation (mean of 8), 278. Calculated for $C_{20}H_{30}O_2$, 302; for $C_{19}H_{28}O_2$ = 288. Acid value, 190·4; saponification value, 202·0; hot, 324·8. To ascertain whether hydrolysis occurred during the saponification process 2 grammes of the acid were saponified in a reflux condenser, the acid separated from the lye, and recrystallized. The acid so prepared exhibited the same crystalline form, the same melting-point, 147°-148° C., as the original acid, and on analysis gave similar figures: C = 79·80; H = 9·75. Acid value, direct, 190·4; saponification value: cold, 252; hot, 325·92. The acid therefore absorbed nothing during saponification nor during reprecipitation. One gramme of acid neutralized 6·8 c.c. $\frac{n}{2}$ KHO = 0·1326, K = 11·70 K in the potassium salt. The formula $C_{20}H_{29}KO_2$ requires 11·47 per cent K. The formula $C_{19}H_{27}KO_2$ requires 11·96 per cent K. The acid is therefore monobasic. One gramme of acid heated under a reflux condenser for an hour neutralized 11·6 c.c. $\frac{n}{2}$ KHO = 0·2262, K = 18·44 per cent in potassium salt. The formula

$C_{20}H_{28}K_2O_2$ requires 22·63 per cent K. It may be assumed that a second atom of potash is absorbed in this way. The acid potassium salt obtained by neutralization of the alcoholic acid solution by alcoholic potash corresponded to the formula $C_{20}H_{29}KO_2.3C_{20}H_{30}O_2$ = 3·12 per cent K. Found, 3·29 K.

Neutral Potassium Salt.—Obtained by boiling a solution of the acid in a mixture of alcohol and ether with excess of potassium carbonate. Found, K = 11·26 per cent. Calculated for $C_{20}H_{29}KO_2$, K = 11·47 per cent. *Silver Salt.*—Obtained by action of excess of alcoholic silver nitrate on alcoholic solution of the acid; a few drops of very dilute ammonia are then run into this mixture. Found, Ag = 26·70 per cent. Calculated for $C_{20}H_{29}AgO_2$, Ag = 26·40 per cent. *Calcium Salt.*—Obtained by adding calcium chloride to a solution of the acid in dilute ammonia. Found, Ca = 6·56 per cent. Calculated for $(C_{20}H_{29}O_2)^2Ca$: Ca = 6·23 per cent. *Lead Salt.*—By precipitation of an alcoholic solution of the acid by an alcoholic solution of lead acetate. Found, Pb = 25·14 per cent. Calculated for $(C_{20}H_{29}O_2)^2Pb$: Pb = 25·44 per cent. Methoxyl value nil. Acetylization test, heating acid with acetic anhydride and anhydrous sodium acetate, and etherification test, passing dry HCl gas through alcoholic solution of acid, both negative. Laricinolic acid forms 4 - 5 per cent of the balsam.

The greater part of the acid resins extracted by soda, 55-60 per cent of the oleo-resin, is amorphous. When after standing for several months the alcoholic acid mother-liquor from the crystallization of laricinolic acid formed no more crystals it was precipitated by very dilute hydrochloric acid. The amorphous acid is then precipitated in white flakes, which are redissolved in alcohol and partly precipitated in the state of lead salt, by an alcoholic solution of lead acetate, the rest of the acid remaining dissolved in the mother-liquor.

This reaction thus separates the crude amorphous acid into two acids, the one giving a precipitate, the other not, with lead salts. These two acids have been designated α-larinolic and β-larinolic, their further study having demonstrated that they are isomers, but not identical; but apart from their action on lead salts in alcoholic solution, their properties are perfectly similar.

a-Larinolic Acid.—Melting-point, 80°-81° C. Optically inactive. Mean of three analyses: C = 78·90; H = 9·72. Calculated for $C_{18}H_{26}O_2$: C = 78·83; H = 9·49. For $C_{19}H_{28}O_2$: C = 79·16; H = 9·73. Acid value, direct, 198·8; saponification value: cold, 238; hot, 316·4. One gramme neutralized 7·10 c.c. $\frac{n}{2}$ KHO. Salt-formation value = 13·84 per cent K. Potassium salt = 12·15 per cent K. Calculated for $C_{18}H_{25}KO_2$: K = 12·5 per cent. For $C_{19}H_{27}KO_2$: K = 11·96 per cent.

β-Larinolic Acid.—Melting-point, 85-86. Optically inactive. Mean of three analyses: C = 78·67; H = 9·68. Acid value, 196;

saponification value: cold, 240·8; hot, 302·4. One gramme neutralized 7 c.c. $\frac{n}{2}$ KHO. Therefore the salt formation value is 12·87 K and the potash salt = 12·01 K per cent.

Potassium hydrate extracted nothing further from the ethereal extract. The resene could not be obtained in a solid form, it constitutes 15 per cent of the oleo-resin. The ethereal oil has a pleasant perfume like mace oil and lavender oil; its density is 0·872. It consists of a lighter volatile oil forming 15·16 per cent of the oleo-resin, boiling between 155° and 170° C., the greater part distilling at 157° C., and a heavier volatile oil, 5-6 per cent of the balsam, and boiling at 190° C. For full analysis see Table XV, p. 74 (larch turpentine).

Larch Overflow Resin.—Bamberger found caffein along with vanillin, and much less ferulaic acid. The resinol lariciresinol is different from the pinoresinol in the black fir and the common fir. Melting-point: impure, 164° C.; pure, 169° C. Mean of 5 + 5 analyses: C = 65·91 and 66·07; H = 6·48 and 6·42 per cent. Calculated for $C_{19}H_{19}O_5$: C = 65·98; H = 5·53. For $C_{19}H_{22}O_6$: C = 65·90; H = 6·36. The molecular weight estimation gave 330, 378, 371, 328, 358, 371, 304. Calculated for $C_{19}H_{22}O_6$, 346. It contains two methoxyl groups. Calculated for $C_{17}H_{16}O_4(OCH_3)_2$, 17·91 per cent. It yields a tetra-acetyl derivative, melting-point, 160° C. Found: C = 62·96; H = 5·85; CH_3CO = 33·43; OCH_3 = 11·36. Calculated for $C_{17}H_{12}(OCH_3)_2(OCH_3CO)_4$: C = 63·03; H = 5·83; CH_3CO = 33·46; OCH_3 = 12·06 per cent, and a tri-acetyl derivative with a melting-point of 92° C. = $C_{17}H_{12}(OCH_3)_2(OCH_3CO)_3OH$. The dimethyl ether = $C_{17}H_{12}(OCH_3)_4(OH_2)$, and the diethyl ether, $C_{17}H_{12}(OCH_3)_2$-$(OC_2H_5)_2(OH_2)_2$, may be similarly prepared.

The resinol, therefore, has the rational formula $C_{17}H_{12}(OCH_3)_2(OH)_4$. It can be converted into an isomer, by boiling with sodium alcoholate, melting at 95-97. Mean of five analyses of this isolariciresinol: C = 65·89; H = 6·48; OCH_3 = 17·72. Calculated for $C_{19}H_{22}O_6$: C = 65·90; H = 6·36; OCH_3 = 17·91. By boiling with benzol it is suddenly converted into a physical isomer, melting-point, 152°-155° C., crystallizing in needles, which gives similar figures. Found: C = 66·18; H = 6·38. Calculated for $C_{19}H_{22}O_6$: C = 65·90; H = 6·35. This isomer reverts to the isomer with melting-point 95° C. by recrystallization from alcohol or alcohol and petroleum ether. Isolariciresinol yields a tetra-acetyl derivative with melting point 169° C., *a*-dimethyl and *a*-diethyl ether. By dry distillation the lariciresinols yield *inter alia* guaicol and pyroguaicol. The diethyl lariciresinol yields by acetylization a diacethyl-lariciresinol, $C_{17}H_{12}(OCH_3)_2$-$(OC_2H_5)_2(OCH_3CO)_2$. Laricinol by hot treatment with alcoholic HCl yields an anhydrous product, $C_{17}H_{12}O_2(OCH_3)_2(OH)_2$. Laricinol, or better, its tetra-acetate, yields on treatment with chromic acid an oxidation product, $C_{17}H_{12}O_2(OCH_3)_2(OCH_3CO)_4$, which yields on saponification a body with the composition $C_{17}H_{10}O(OCH_3)_2$, melting at 180°-181° C.

"*Artificial*" *Venice Turpentine* (Andés).—The manufacture of artificial turpentine is simple, the materials consisting of very light rosin and pale rosin oil, the former being melted and stirred up in the oil until dissolved, the proportions being selected so as to furnish the proper turpentine consistency. So far as the price will allow, the smell may be improved by adding a little elemi, very small quantities of ethereal oils, especially citronella oil, carraway oil, etc., or even oil of turpentine, the latter approximating the product to the smell of natural turpentine. The fluid mixture is carefully strained, to remove all solid matters, before the addition of the essential oils.

The following recipes are recommended:—

	Parts by weight.		Parts.
1. Very pale rosin	50	3. Very pale rosin	50
Rectified rosin oil	25	Elemi	5
Citronella oil	½	Oil of turpentine	14
	Parts.		
2. Very pale rosin	50	4. Very pale rosin	50
Rectified rosin oil	20	Oil of turpentine	14
Elemi	5	Pinolin (rosin spirit)	8

5. *Bisco's Process.*—Forty parts of rosin oil are warmed in the air (air blast) until the weight has diminished by 10 per cent, and are then treated with 50-60 parts of rosin and 4-5 parts of oil of turpentine, followed by a solution of 0·2-0·3 parts of alkali hydroxide or alkali carbonate (or a suspension of alkaline earth hydroxides) in 10-12 parts of water. The product is more tacky than natural turpentine, and may be exposed to the air for a long time without hardening. The proportions may be modified according to the consistency desired. For producing the acid rosin soaps, the alkalis may be replaced by oxides of the alkaline earths or other metals. A portion of the rosin oil may also be replaced by a heavy petroleum hydrocarbon, to furnish a product of still less drying power for certain purposes.

According to Schaal, coniferous resins are distilled at about 270° C. under reduced pressure (60-70 cm.). The aqueous and oily portions of the first distillate are separated and the operation is continued up to 310° C., a thin stream of oil of turpentine (about 2-4 per cent of the weight of resin) being introduced through a narrow tube into the molten mass in the still, which is preferably fitted with stirrers. Two receivers are provided, the heavy turpentine condensing in the first one, which is kept at a temperature of 140°-160° C. by cooling the still pipe or heating the receiver. This causes the added oil of turpentine to pass over into the second receiver, where it is condensed by a cooling medium.

For "Venice" turpentine as made in France, see p. 81.

CHAPTER VII.

SOURCES AND METHODS OF OBTAINING TURPENTINE.

5. *Obtaining American Turpentine.*—The most valuable oleo-resiniferous pine in the United States is the long-leaf pine (*Pinus Australis, Pinus Palustris*).[1] Upon this pine (see p. 44) depend more or less a number of industries, chief of which is the extraction and elaboration of spirits of turpentine and rosin and their various derivatives.

In establishing a turpentine orchard and still, two points require consideration —transport facilities to shipping points, and an adequate supply of water for the condenser connected with the still. The copper stills generally used have a capacity of about 800 gallons, or about twenty to twenty-five barrels of crude turpentine. To charge such a still twice in twenty-four hours during the working season, 4000 acres of a good average stand of pine timber are necessary. This area is divided into twenty parcels, each of 10,000 boxes, as the incisions are called, which are cut into the tree to receive the exuding oleo-resin. Such a parcel is termed a crop, constituting the allotment to one labourer for the task of chipping. When boxing was in vogue the work in a turpentine orchard started in the early part of the winter with the cutting of the "boxes". Until a number of years ago no trees were "boxed" of a diameter less than 14 inches. Of late, however, saplings less than 10 inches in diameter are gashed. Trees of full growth, according to their circumference, receive from two to four boxes, so that the 10,000 boxes are distributed among 4000-5000 trees in an area of 200 acres.

The flow of the crude oleo-resin was stimulated by stripping the tree of its bark and collecting the exuded resin in peculiar V-shaped receptacles called "boxes" cut out of the trunk of the tree. The trees are boxed during the fall and winter, the legal limit being from 15 November to 15 March. The lower lip of the box is horizontal, the upper arched, and the bottom of the box is about 5 inches below the lower lip and 8-10 inches below the upper. This somewhat barbarous method of procedure now to be described has lately given way to some extent to the French cup and gutter system (see p. 63).

The boxes are cut from 8-12 inches above the base of the tree, 7 inches deep, and slanting from the outside to the interior, with an

[1] Not to be confused with the Himalayan *Pinus Longifolia* (p. 63), which is quite a distinct species.

angle of about 35°. In the adult trees they are 14 inches in the greatest diameter and 4 inches in the greatest width, with a capacity of about three pints, but the capacity varies from ½-1 gallon. The cut above this reservoir (or box) forms a gash of about the same depth and about 7 inches in its greatest height. Some operators cut larger boxes than others, and as the trees are often boxed in one to four places at a time, according to the size of the tree, many die off during the first or second year. But medium-sized boxes pay best; the flow is as great and the duration longer. In the meantime the ground is laid bare around the tree for a breadth of 2½-3 feet, and all combustible material loose on the ground is raked into heaps to be burned, in order to protect the trees from the danger of catching fire during the conflagrations which are frequently started in the pine forests by design or carelessness. The employment of fire for the protection of turpentine orchards against the same element necessarily involves the total destruction of the smaller tree growth, and if allowed to spread without control beyond the proper limit often carries ruin to the adjoining forests.

Cornering the Pines.—As soon as the boxes are cut the oleo-resin begins to flow, and by the time the boxes are all cut and cornered the oleo-resin in the boxes is ready for dipping. The boxes are cornered by cutting a strip from each box with an adze.

Chipping the Pines.—During the early days of spring the oleo-resin begins to flow, but as the wound made in "boxing" soon heals the surface is again scraped and chipping is begun; that is to say, the tree is gashed or chipped so as to remove the surface bark above the box and lay bare the youngest layers of the wood to a depth of about 1 inch from the outside of the bark to a height of about 3 feet above the box.

The removal of the bark and of the outermost layer of the wood —the "chipping" or "hacking"—is done with a peculiar tool, the "hacker," which is a strong steel knife with a curved edge, fastened to the end of a handle bearing on its lower end an iron ball of about 4 lb. in weight, which acting as a lever gives increased force to the stroke inflicted upon the tree, and thus lightens the labour of chipping. The sharp edge of this tool is so turned that it cuts a streak from the tree of the exact size requisite to start the flow of oleo-resin, viz. ¾ of an inch wide and ¼ inch deep. The operator standing in front of the box commences at the top and cuts his streaks obliquely from right to left and left to right, thus giving to them a sort of L or V shape. The trees are scraped in this manner every eight or ten days from October or November, extending generally through a period of thirty-two weeks, and the weight of the chip is increased about 1½-2 inches every month. The surface and pores of the wood exposed by the previous hacking in the interval between the two hackings becomes clogged up by the evaporation of the essential oil from the exuded oleo-resin. But a very small shaving is all that is required to restart the flow. The resin which accumu-

lates in the boxes is dipped into a pail with a flat trowel-shaped dipper —a peculiar sort of spoon or ladle which fits into the bottom of a box. The dipper is emptied into a bucket and the bucket when full into a barrel, the operator leaving it to drain while he fills another bucket. The barrels when full are hauled by wagons to the still. In the first season from six to eight dippings are made. The 10,000 boxes yield at each dipping about forty barrels of "dip" or "soft gum," or about 240 lb. net weight. The flow is most copious during the height of the summer (July and August), decreases with the approach of colder weather, and ceases in October or November. As soon as the exudation of the resin is arrested and it begins to harden under the influence of a lower temperature, it is carefully scraped from the gashed surface of the tree and the boxes with a narrow, keen-edged knife attached to a long wooden handle.

In the first season the average yield of dip amounts to about 280 barrels, and of the hard "gum" or "scrape" to about seventy barrels. The first yields 6½ gallons of turpentine to the barrel of 240 lb. net, and the latter 31 lb. to the barrel, resulting in the production of 2100 gallons of spirits of turpentine, and 260 barrels of rosin of the higher and highest grades. The dippings of the first season are called "virgin dip," from which the finest quality of rosin is obtained. In the second year from five to six dippings are made, the crop averaging 225 barrels of "soft turpentine" and 120 barrels of "scrape," making altogether about 1900 gallons of spirits of turpentine. The rosin, of which about 200 barrels are produced, is of a lighter or deeper amber colour, and perfectly transparent, and of medium quality.

In the third and fourth years the number of dippings is reduced to three. With the flow over a more extended surface the turpentine thickens under a prolonged exposure to the air, and loses some of its volatile oil, partly by evaporation, and partly by oxidation. In the third season the dip amounts to about 120 barrels, yielding about 1100 gallons of spirits of turpentine and 100 barrels of rosin of a more or less dark colour, less transparent than that of the second year, and of poorer quality. In the fourth year three dippings of a smaller quantity of soft turpentine than that obtained in the previous season and about 100 barrels of scrape are obtained, with a yield hardly realizing 300 gallons of spirits and 100 barrels of rosin of the poorest quality. As a general rule the flow of resin from the tree after having been boxed for four or five years is not sufficient to be remunerative. The oleo-resin is poor and contains but a small proportion of essential oil. On the other hand, however, the trees are sometimes scraped to such a height that they cannot be reached by the hack and are then scraped by an instrument with a long handle called a puller. But a crop does not yield so much by pulling as by chipping. The higher the boxes are chipped the greater is the yield. They are sometimes, but rarely, wrought to the height of 15 feet, and ladders become necessary to hack the trees afresh. In such cases

the oleo-resin on its way to the boxes solidifies partially on the trunk of the tree and has to be scraped off. When dead the tree is sawn into lumber or cut up for its tar and wood turpentine. Although the tapped wood is less appreciated, and often rejected by engineers as weak and faulty, it would appear by direct experiments by the U.S.A. forestry officials that it is, if anything, superior in this respect to untapped timber.

6. *Indian Turpentine.*—(1) *Pinus Excelsa,* Wall (Indian blue or five-leaved pine). Evergreen tree of temperate Himalaya, at altitude of 6000-12,500 feet, goes westward to Kafristan and Afghanistan, eastward to Bhutan. Wood highly resinous, yielding turpentine and tar. Tapped by vertical cuts as P. longifolia, *vide infra.* Tapped for three years, let rest another three, and tapping recommenced on other side. (2) *Pinus longifolia,* or the "long-leaved pine," the most important of the Indian pines from the present point of view, is a large, gregarious, more or less deciduous tree growing chiefly on the dry Himalayan slopes (outer Himalaya and Siwalik Ranges, 1500 to 7500 feet, extending west to Afghanistan and east to Bhutan). In North-west India, including Kashmir and the Native States, it covers an area of 2000 to 4000 square miles, and its turpentine is more freely collected and used than that of any other Himalayan conifer. The tapping of this species (according to Watt) in a systematic manner was commenced in Jaunsar, but has now extended both to the Punjab on the west and to the forests of Kumaon on the east. In 1889 about 9600 trees were tapped in Jaunsar, each giving about 8½ lb. of resin. The total yield of the year was over 1000 maunds of resin which produced at the Forest School factory, Dehra Dun, about 900 maunds of rosin and 1740 gallons of turpentine, which sold for nearly R9000. There are two methods of tapping the tree, native and European. The system employed by the hillmen of Kumaon and Garhwal is to cut a niche[1] into the trunk about 3 feet from the ground, the bottom of which is hollowed out. The oleo-resin is collected as the niche fills, sometimes every second or third day, usually between the fourth and fifth days. The niche has to be deepened and lengthened from time to time, and it may be used for two or even three years. By the European method an incision about 1 foot long, 4 inches wide, and 2 inches deep at the base, not including the bark, is cut into the tree, and a curved incision about 5 inches long is made just below that, into which a piece of zinc is inserted so as to form a lip from which the resin may flow into a pot suspended beneath. The turpentine oil obtained from it is reported to be of good quality, but has a tendency to darken in colour, and leaves a considerable residue on distillation. These defects are no doubt due to careless preparation, and can probably be remedied.

(3) *Pinus gerardiana,* Wall, is a moderate-sized evergreen tree, found principally on the inner, dry North-west Himalayas and in

[1] Cf. American "box," p. 60.

Garhwal, generally at an altitude of 6000 to 12,000 feet, the mountains of Northern Afghanistan and Kafristan, also Hareab district, at 7000 to 11,000 feet. According to various reports it affords an abundant supply of a fine turpentine oil. The wood is hard, durable, and very resinous, but rarely utilized since the tree is so highly valued for its almond-like seeds which form a staple food.

(4) *Pinus khasya* Royle, a large evergreen tree, one of the principal Indian pines, is widely distributed on the Khasia hills, Chittagong hills and the hills ot Burma, at a height of 3000 to 7000 feet. The turpentine oil obtained from its oleo-resin was examined for the Imperial Institute by Prof. Armstrong in 1896, who reported favourably on it. The crude turpentine, which is a grey, thick, pasty mass, furnishes by distillation with steam 13 per cent of its weight of oil. The original turpentine oleo-resin has a slight but agreeable odour, less pronounced than that of French turpentine, and Armstrong describes the oil as of the highest quality, capable of serving every purpose to which spirits of turpentine, French or American, are put. Samples submitted to a London firm of brokers were valued at £4 to £6 per ton for the crude turpentine, £24 for refined spirit, and rosin £5-6 per ton. But at the present day these prices would be greatly enhanced by the great rise in price of both turps and rosin.

(5) The only other Indian pine of importance is *Pinus Merkusii*, of the Shan States, Martaban, and Upper Tennasserim, at 500 to 3500 feet. Although the turpentine oil produced by it is dear, owing to the small quantity available, there is no doubt that the area of growth could be considerably increased. The resin of this species, says Watt, was examined by Armstrong at the same time as that of *Pinus khasya*. The crude turpentine is more fluid and clearer, and yields nearly 19 per cent of oil. The two oils closely resemble each other in all respects, and correspond exactly in their properties to French oil of turpentine.

(6) *Deodara oleo-resin.*—The Cedrus Libani Var. Deodara is *in India* a very large evergreen tree, often 250 feet high, from Afghanistan Mountains to Dauli River in Kumaon. Immune from white ants, its wood is the chief timber of India—that of some buildings in Kashmir being 600-800 years old. The oil resembling crude turpentine is obtained from the wood, and is employed by the men who float deodar logs to coat the skin buoys by which they pass the rapids. Metallic articles kept in a box of deodar wood are beautifully varnished by the action of the oleo-resin (Watt).

(7) *Turpentine of the Aleppo Pine.*—This somewhat handsome tree, *Pinus halepensis*, bears few leaves, but they are long and fine and of a glaucous green, two or three being enclosed in the same sheath. It grows in Provence, Spain, Syria, Barbary, Tunis, and Algeria. In Tunis the Aleppo pine is important. All the limestone mountains to the north of Medjerda, where some forest tracts still remain, are covered by it to the extent of 450,000 acres. It is hardy, grows in all soils, even the most arid, and at all exposures and altitudes, from

sea-level to the most elevated point in Tunis, the top of Djebel Chanbi. The Aleppo pine thus grows in spots not only unfit for farming but which suit no other tree. It, however, generally only forms thin plantations of badly developed, twisted, and mutilated trees, which on distillation yield turpentine, rosin, and tar of the usual quality. In the second forest, with over a million resiniferous trees, the production is trebled, 6000 quintals of turpentine oil and 12,000 quintals of rosin. An unleasable tract of forest, Khars and Ksenne, near Aumale, has already fixed the attention of speculators. It comprises over 20,000 Jochs of land with over a million resiniferous trees, of which 100,000 still standing are killed by rosin. The following other Algerian forests are in good condition for resin exploitation: Ouled Hama with 3000 acres, on the Medsak road, near Boghar; various tracts in the Milianah Inspection, with over 20,000 acres; Guarancenos with 2250 acres; Lelamata with 3325 acres; Oued Tolta with 6750 acres. Another rosin distillation establishment could be made at Ben Salah, 7500 acres; El Dekera, 47,500 acres; Senkel Hana, 22,675 acres, south from Orleansville.

7 (*a*) *Sicilian Aleppo Pine Oil.*—When rectified in a current of steam over anhydrous potassium carbonate, a sample of Sicilian spirits of turpentine from *Pinus halepensis* had a specific gravity of 0·858 to 0·863 at 20° C.; optical rotation, + 25° to + 30°; and refractive index, 1·4664 to 1·4684 at 20°. On treatment with a current of dry hydrochloric acid gas, it yielded 25 per cent of a solid and 75 per cent of a fluid monohydrochloride. It is said to be employed for the adulteration of the cheaper varieties of lemon oil. It may be noted, however, that the oil is dextro-rotatory up to + 30°, whilst, according to Fernandez, the Spanish turpentine oil derived from this source is levo-rotatory.

7 (*b*) *Spanish Aleppo Pine Oil.*—According to Fernandez the essential oil from the balsam of *Pinus halepensis*, a pine tree common to Spain, differs in its characters from the turpentine of France and the United States. A typical oil rectified with steam had the following characters:—

Specific gravity at 15°	0·8620
" " 20°	0·8590
Optical rotation	− 8·73°
Refractive index at 20°	1·4654

On treatment with dry hydrochloric acid gas, it yielded 35 to 40 per cent of a solid monohydrochloride, and 60 to 65 per cent of a liquid hydrochloride. The latter could be easily converted into borneol by means of metallic magnesium. A well-defined nitrosochloride of the pinene present was obtained, melting at 95°.

7 (*c*) *Algerian and French Aleppo Pine Oleo-resin.*—Three samples of the turpentine of the Aleppo pine (*Pinus halepensis*) from the South of France and Algeria have been examined by Vézes, who obtained the following results:—

Oleo-resin :—

	Per cent.
Essential oil	14·7-27·0
Non-volatile (rosin)	66·7-78·3
Solid impurities	0·8- 6·6
Water and loss	2·1- 5·5

Essential oil :—

Density at 25° C. . .	0·8552-0·8568
Optical rotation $[\alpha]_D$	+ 46·6° to + 47·6°
Refractive index at 25° .	1·4638-1·4652

By the redistillation of the essential oils at least 80 per cent in each case passed over at a temperature of 155° to 156° C., and these had the following characters :—

Density at 25° C. . .	0·8541-0·8547
Optical rotation $[\alpha]_D$	+ 47·4° to + 48·4°
Refractive index at 25° C. .	1·4633-1·4639

These oils differ from ordinary turpentine in their lower gravity and in their action upon polarized light. It is estimated that *d*-pinene is present in the oil of Aleppo pine to the extent of at least 80 per cent, and that it therefore constitutes a good raw material from which this terpene may be obtained.

8. *Swedish Turpentine Oil.*—Kondakow has investigated the oil of turpentine distilled from Swedish pines. He finds it to be dextro-rotatory. By fractional distillation he obtained a fraction which boiled between 153° and 160° and was highly dextro-rotatory, + 22°; the fraction boiling between 185° to 190° was also dextro-rotatory, + 10°. The author claims to have isolated sylvestrene from the oil, but the characters are not those given by Wallach in his classical research. The following table shows the differences :—

	Kondakow.	Wallach.
Specific gravity	= 0·854	0·851
Boiling-point	= 174°-176°	176°-177°
Refraction index	= 1·49013	1·47470
Optical rotation	= nil	+ 66°

9. *Hungarian Fir Resin.*—According to Augustin, a resin is obtained in Hungary from *Picea montana* (Schir), and is sold in packages wrapped in the bark of the tree. The yield of resin from this tree is greater than that from the spruce fir (*Picea excelsa*), but the method of collection leaves much to be desired. Attempts are being made to remedy this state of affairs. The product of *Picea excelsa* (Table XV, p. 74) is Burgundy pitch, or white pitch. Another white pitch is obtained in Russia from *Abies pichta* or *Abies Sibirica*, while Canada balsam is the product of *Abies Canadensis*. A product similar to this from Hungary is obtained in the Jura from *Picea excelsa*. The latter

contains about 32 per cent of an essential oil, while the solid resin consists principally of resin acids, notably Picea-pimarolic acid ($C_{25}H_{44}O_2$), which is amorphous and soluble in a solution of sodium carbonate.

10. *Chian Turpentine—Botanical Source; Geographical Origin.*—Although the term turpentine was first applied to this oleo-resin, it is not derived from a conifer. It is the product of an anacardiacea, *Pistacia Terebinthinus*, the terebinth tree, a tree or shrub growing in the Island of Scios, district of Papho, and in Cyprus, and common on the islands and coast-lines of the Mediterranean. *Occurrence in the Plant; Collection and Preparation.*—During May and June the bark is incised, the oleo-resin is collected, boiled, and kneaded with water. Pasqua describes the incisions as being made in August. The oleo-resin begins to flow within a day, and it is purified by melting in the sun. The oleo-resin occurs in the secretion vessels of the bark. *Chemical Composition.*—The balsam has not been exhaustively examined. It contains 83-88 per cent of resin, 9-12 per cent of dextro-rotatory, + 12·6 to + 19·45° essential oil and traces of succinic acid. The density of the essential oil is 0·868-0·869. It consists of pinene. According to Power two modifications of borneol derivative are present, one the acetic ether and the other the valerianic acid ether. An indifferent neutral substance of the formula $C_{18}H_{30}O_2$ is also described.

Specification—Density.—The density of the oleo-resin is 1·050. But both density and consistency vary with the percentage of essential oil. *Taste.*—Faint aromatic like pine turpentine but neither sharp nor bitter. *Smell.*—Aromatic like pine turpentine. *Solubility.*—Almost completely in the usual resin solvents. *Optical Deviation.*—Of the oleo-resin, levo-rotatory; that of the essential oil, dextro-rotatory (*vide supra*). *Microscopical Examination* (distinction from pine oleo-resins)—Plant debris if present should show no pitted vessels indicative of pine oleo-resin, and the turpentine itself should exhibit no crystals which would also point to the presence of pine oleo-resin. Acid value, 47·8-53·4 (Kremel), 47·13-48·53 (E. Dieterich). Ester value, 19·13-21·47 (E. D.). Saponification value, 66·26-70·00 (E. D.). Landerer found the oleo-resin adulterated with 20-30 per cent of sand and pebbles.

11. *Resinous Balsam of Pinus Sabiniana.*—The resinous exudation from the nut or digger pine has been examined by Kremers, Rabak, and Sievers. The sample was collected in California, was semi-solid, had a dirty brown colour, and a characteristic, pleasant odour. It was contaminated with pieces of bark and other materials. The acid equivalent was found to be 127, and the ether equivalent 37, figures which approximate closely to those of ordinary resin. By distillation in a current of steam the balsam yielded 7·3 per cent of an essential oil, which was nearly colourless, and had an odour somewhat like that of the orange. Pinene could not be detected in this oil, the principal constituent being normal heptane (C_7H_{16}), a hydrocarbon of the paraffin series; 50 per cent alcohol extracted from this oil a

golden yellow product having a very pleasant odour; the latter had an acid value of 42, and an ester volume of 124. The residue obtained after distillation of the balsam was hard, brittle and opaque, and had an acid value of 142. Heptane was found to be present in the oil from *Pinus ponderosa*, by Thorpe, and his results were confirmed by Schorlemmer, who proved that the heptane obtained from this oil was the same as that contained in petroleum spirit.

12. *Norway Pine Oleo-Resin.*—According to Frankforter the oleo-resin of the Norway pine (*Pinus resinosa*) (p. 44) has a specific gravity of the natural product of ·8137 at 20° C. compared with water at 4° C. The optical rotation was $[a]_D$ at 20° C. = + 4, and the refractive index 1·4788 at 20° C. The volatile oil removed by distillation in a vacuum amounted to about 20 per cent. The rosin left in the retort melted at 81·5° C. It was very soluble in absolute alcohol, acetone, benzene, toluene, and xylene. In alcohol of 70 per cent it was only slightly soluble, and in 60 per cent alcohol it was quite insoluble. On dissolving this rosin in ether and pouring the solution into 80 per cent alcohol, a crystalline body separated with a melting-point of 83·7° C. containing 72·62 per cent of carbon and 9·24 per cent of hydrogen. This was separated into two substances, one of which formed an unstable ammonium salt $(NH_4)_2C_{25}H_{36}O_5$, melting at 98°-112° C., from which the acid was obtained, which after recrystallization from 80 per cent alcohol, had a melting-point of 97° to 98° C., with a composition of $C_{25}H_{36}O_5$. The second substance was common abietic acid, but the melting-point was lower than usual (129° to 130° C.). Abietic acid or an isomeric acid is present in most resins, but it is probably accompanied by other acids, which impart characteristic properties. The above resin acid differs from all others, and may be regarded as a new substance, though in some respects it resembles the palabietinic acid of Tschirch.

13. *British Honduras.*—Towards the end of 1904 the Government of British Honduras accepted an American offer to pay one cent each for the privilege of tapping 12,500,000 pine-trees for turpentine. This concession is granted for twenty-six years, and all the pine products obtained will be exempt from export duty. About one-third of the colony is said to be covered with pine ranges consisting almost wholly of *Pinus cubensis*. Nothing is known as to the yield of turpentine obtainable from this species of pine nor as to the quality of the oil yielded by it.

As a sequel, for the first time in recent years turpentine figures as a small amount in the exports from Honduras, the value being £120. But for the difficulties of transport this might be an article of considerable importance. As it is, however, many of the pine forests where it can be obtained are in the heart of the country, and the expense of conveyance to the coast makes it impossible to export this product with advantage.

14. *Mexican Turpentine.*—A turpentine distilling plant, with a capacity of 200,000 gallons per annum, has been erected near

Morelia, in the State of Michocan. This undertaking constitutes the beginning of the Mexican oil of turpentine industry, the object of which is to utilize the extensive forests of long-leaf yellow pine found in that country.

15. *Turpentine in Japanese Sakhalin.*—The British Vice-Consul at Hakodate reports that experiments, with successful results, have been made under the auspices of the Government of Japanese Sakhalin in the extraction of turpentine from the "todo-matsu" (*Abies sachalinensis*) and another species of pine. These trees flourish in great numbers in Sakhalin, and, as the manufacturing process is apparently simple, there is reason, says the Vice-Consul, to believe that a valuable industry will develop. After the extraction of the crude oil by incisions in the bark, the trees themselves are felled and used for timber. It is stated that the total amount of wood available is about 60,000,000 cubic tons, and that it is proposed to deal with this on the system of a hundred years' rotation, felling thus at the rate of 600,000 cubic tons per annum. Treated in this manner, it is believed that the supply will be virtually inexhaustible.

16. *The Production of Russian Turpentine.*—The largest quantity of Russian turpentine is produced in Poland, where the peasants are engaged in this industry, employing the following primitive methods: Pine stumps are placed in trenches dug in the ground, these trenches having iron-sheeted bottoms, under which fires are started to distil the turpentine from the stumps by means of the heat. The turpentine so extracted is caught in reservoirs, and through a pipe line conducted to the place where it is placed in barrels and shipped to the nearest town to be sold. It is impossible to ascertain the cost of running these plants. The raw turpentine is not sold at the place of production. There are three grades of turpentine sold in the market. The price of each of the grades is at present quoted as follows: Best quality, 2·80 roubles per pood, or 4 cents per lb.; second quality, 2·50 roubles per pood, or 3 6.10 cents per lb.; the lowest grade, 1·80 roubles per pood, or 2 6.10 cents per lb. —all products in this country being sold by weight.

17. *Pinus Maritima, the Landes Pine, Maine (France) Pine, Pinus Maritima* (Lamarck).—(*a*) *The Maritime Pine in Europe.*—The geographical range of the maritime pine, a tree of temperate climates, is very wide. Here and there it has been acclimatized in Britain for shelter or ornament, but its native habitat includes the Mediterranean shores and hinterland of France, Italy, Algeria, Corsica, the shores of the Bay of Biscay, and Spain. In Gascony this tree covers 1,875,000 acres of land, or an area almost equal to the whole of Argyllshire. Wide tracts of maritime pine are also met with in the lower Pyrenees, on the shores of Saintogne, in Dordogne, Brenne, Sologne, and Maine. It will thus be seen that the maritime pine is a tree of temperate climates. The tree is, in fact, so sensitive to cold that the foresters of Sologne will long remember the havoc played in their pine woods by the severe winter of 1879-80. (*b*)

The Maritime Pine in Africa.—In Africa it forms immense forests near Bône and Cape Bangaroni. It is also found on the north-west coast of Khroumirie, Tunis, upon the mountains situated near Taharka, and the Algerian frontier; it there covers an area of 75,000 acres. The pine groves burnt in 1881, upon the entry of the French troops into Khroumirie, are already re-afforested, being composed largely of young stocks, which dominate the reserves spared by the fire. (*c*) *The Maritime Pine in the Landes: Profit and Loss.*—The best trees are grown from seed, hence this is the usual method of rearing the tree. The seed is sown broadcast and the plantation is thinned every four or five years by felling the poorer trees, so that after twenty to thirty years the trees are at least 6 feet apart. If there be still some trees to be felled to separate the remainder by that distance, they are

FIG. 6.—Collecting turpentine oleo-resin in France.

incised deeply on each side, and the resinous exudation collected in the usual way. Left thus the tree withers and is felled within four or five years. The best trees are then chosen, and the others treated exhaustively, as before. The selected trees are left 27 feet apart, and the collection of the oleo-resin from these is conducted less exhaustively. They are not tapped until at least 12 inches in diameter. The maritime pine loves a light, loamy soil; it does not succeed in too damp ground but it thrives in the sand of the Landes, as pure and fine in certain spots as silver sand, so long as the layer of drift is neither too superficial nor too impermeable. But the maritime pine has not only the advantage of thriving in poor, sandy soils, but in virtue of its light foliage and its denuded trunk it resists the wind well in exposed situations. It has therefore been used from the most remote antiquity for fixing the shifting sands of the Gascony dunes. About the end of the eighteenth century Peyscha Dubose, Desbin

Brothers, and, *after them*, Bremontier, established the best methods of planting the dunes, although Bremontier generally gets the whole credit as being the first to adopt this peculiar mode of stopping further encroachments on the land. The tree grows rapidly; when thirty years old it is 40 inches in girth, at the height of a man from the ground. The slender cime lets the light reach the ground, on which is a dense growth of moss, heather, rushes, etc., which turf is used as litter or sometimes distilled. So copious and precocious is

FIG. 7.—Collecting the turpentine oleo-resin by the cup and gutter system from the maritime pine in France.

the secretion that the thinned trees are incised for their resin by their fifteenth year. But fire often devastates the forests. The causes are many and varied—*inter alia*, carelessness in weed-burning, the use of matches, touch-paper, sparks from locomotives; even arson is not unknown. Again forests are often invaded by the caterpillar *Cnethocampa pityocampa*, which devours the needles and greatly lessens the production of timber and resin.

Rosin and Turpentine Production in France.—A far greater proportion of turpentine and pale rosin is obtained by the careful French

method of tapping the pine-trees and refining the product than is got in the United States. A "face" is made by removing the bark of the pine (*Pinus maritima*), at the base of which a cup is placed to collect the gum which flows therefrom. The gum is conducted into the cup by two "gutters" placed in a V shape. Every year the bark is removed from higher up the tree, and the cup and gutters moved up to the new "face". The gum is collected in barrels and

FIG. 8.—Collecting turpentine oleo-resin in France.

taken to the factory, where it is put into a boiler to remove the particles of foreign matter—chips of wood, leaves, insects, etc. It is then placed in a still and the distillation results in turpentine, the residue being rosin. The latter is packed in casks containing about 400 kilos (8 cwt.). Care is taken not to cut too many "faces" on the pine, unless it is intended to kill the tree in order to thin the forest, so that in France the pine can be tapped for forty years or longer, whereas in America after four years of turpentining the pine forest is given over to the lumber mill.

The Exploitation of the Maritime Pine for its Oleo-Resin in Greece.—The American process is followed. The tree is cut to the centre to the height of a metre, and much resin flows, and the tree falls to the ground the first storm that occurs. The Grecian oleo-resin came to market through Trieste and Marseilles, but owing to the amount of sand and other impurities found few purchasers. Latterly there are coming to market much larger quantities of very pale oleo-resin and turpentine which would seem to imply that the industry is now in a flourishing condition.

Composition of Turpentine Oleo-Resin.—Method of analysis: Tschirsch dissolves 50 grammes of oleo-resin of known origin in 500 c.c. of ether. Water and impurities separate. The ethereal solution is agitated with a 1 per cent ammonium carbonate solution, the fractional extractions, repeated several times, bringing the ethereal solution each time to its original volume. The aqueous liquors obtained, decomposed by dilute hydrochloric acid, give a precipitate of resinic acids. Fractional extractions are then made with a 1 per cent sodium carbonate solution and the aqueous liquids treated in the same way. The residue, insoluble in alkaline carbonates, is freed from ether, distilled with water, yielding essential oil and neutral resin or resene. Succinic acid is determined by dry distillation on a sand-bath. The bitter principle is dissolved by hot water.

TABLE XIV*a*.—ANALYSIS OF BORDEAUX TURPENTINE OLEO-RESIN (TSCHIRSCH).

Portion Soluble in Na_2CO_3, about 64 per cent.	Per cent.	Portion Insoluble in Na_2CO_3.	Per cent.	Various Substances, about 2 per cent.
Pimaric acid	6-7	Essential oil, volatile portion	25-26	Traces of succinic, formic, and acetic acids, colouring matter, water, and impurities
"	8 10	Essential oil, less volatile portion	3-4	
A Pimarolic acid, B Pimarolic acid	48-50	Bordo resene	5-6	

Tschirsch, Brunning, and Weigel have found acids, some crystalline, others amorphous, soluble in ammonium carbonate; others, soluble in sodium carbonate, occur in all turpentine oleo-resins. The essential oils estimated by distillation often include small quantities less volatile than the bulk. The resenes (neutral resins, abieto resene, bordo resene, etc.) can generally be purified to a white powder when a formula is given them, but Bordo resene remains pasty and its exact composition cannot be determined.

TABLE XV.—COMPOSITION OF TURPENTINE OLEO-RESINS (TSCHIRSCH).

	Maritime Pine. Per cent.	Spruce. Per cent.	Silver Fir. Per cent.	Abies Canadensis. Per cent.	Larch. Per cent.
Resinic acids	64	53	56-60	63	60-64
Essential oil	25-29	30-33	28-30	23-24	20-23
Resenes	5-6	10-12	12-16	11-12	14-15
Various substances	1-2	1-2	1-2	1-2	2-4

Resin Acids from Oleo-Resin from Various Species of Pinus, etc.—The resin acids in the oleo-resin of *Pinus sylvestris*, and other species of *Pinus*, etc., in rosin, galipot, and pine oleo-resins generally, is according to Schkateloff sylvic acid, with three isomeric modifications:—

	Character.	Melting-point.	Optical Rotation.
α-Sylvic acid	White cryst. powder	143°-144°	$[\alpha]^D$ – 73·67°
β-Sylvic acid	Cryst. in three-sided plates	160°	– 92·5°
γ-Sylvic acid	Cryst. long needles, or three-sided plates	179°-180°	Inactive

β-sylvic acid is probably identical with the abietic acid of Mach, and γ-sylvic acid is similar to Laurent's pyromaric acid. Besides crystalline acids, all the oleo-resins contain an uncrystallizable yellow acid, Unverdorben's pinic acid. The formula of the above acids is probably $C_{20}H_{28}O_2\ \frac{1}{2}H_2O$ (or $C_{40}H_{58}O_5$).

The following oleo-resins were examined by Schkateloff:—

TABLE XVI.—SHOWING PERCENTAGE AND PHYSICAL PROPERTIES OF OIL IN OLEO-RESIN FROM VARIOUS SPECIES OF CONIFERS.

A (SCHKATELOFF).

Tree.	Volatile Oil by Steam Distillation. Per cent.	Density of Oil at 15° C.	Optical Rotation of Oil.	Nature of Acid.
Pinus sylvestris	15-16	0·867	+ 22°-24°	α-sylvic
,, abies excelsa	about 13·4	0·873	– 13·2°	α-sylvic
,, cembra	6	8·865	+ 14·04°	—
,, ,,	14, B.-pt. 155°-156° C.	—	+ 17°	β-sylvic
,, taurica	20	0·861 at 19° C.	– 75·9°	α-sylvic
,, strobus	Similar to that of ordinary pine	—	—	α-sylvic
Larix sibirica	14·3	0·870 at 19° C.	– 14·3°	β-sylvic
Abies ,,	20	0·8751 at 19° C.	– 35·6°	non-crystalline

B (TSCHIRSCH).

Source of Oleo-Resin.	Essential Oil. Per cent.	Boiling-point Essential Oil. °C.	Density.	Index of Refraction.	Optical Deviation.
Pinus sylvestris, Russian	15	155-163	0·840	1·473	+ 16·1
,, maritima, French	28-29	150-175	0·865	1·466	– 37·5
Larix Europea, Venetian	15-16	155-170	0·872	1·467	– 13·1
Pinus Laricio, Austrian	35	155-160	0·872	1·466	– 38·5
Picea vulgaris, Burgundy pitch	32-33	—	—	—	—
Pinus palustris, American	20-22	155-172	0·864	1·470	+ 6·9

CHAPTER VIII.

DISTILLATION OF TURPENTINE.

Valuation of Crude Turpentine Oleo-Resin: French Method.—The oleo-resin as it is freshly exuded by the maritime pine is a transparent liquid, but soon becomes turbid, milky, and viscous in contact with air. The commercial article has the consistency of honey, is turbid and granular. After prolonged deposition it forms two layers, the upper a limpid, thick liquid, the lower, solid, exhibits under the microscope a mass of small granular crystals. This deposit redissolves on heating and does not reappear for some time. Bordeaux turpentine oleo-resin possesses a somewhat unpleasant smell and a bitter, nauseous taste. Crude turpentine oleo-resin yields on an average the following products: Turps, 18 per cent; dry resin, 70 per cent; water, 10 per cent; solid impurities, 2 per cent.

The solid impurities consist of sand, shavings, debris of wood and bark, pine needles, insects, etc. The value of the turpentine is evidently in a direct ratio with its percentage of marketable products (of superior quality spirits of turpentine and of pale rosin free from dust, dirt, and grit). In the same way it is in inverse proportion to the amount of water and solid impurities which not only usurp the place of useful products but render the clarification in the turpentine stills difficult and tedious, absorb heat, char, and darken the rosin. A technical valuation includes four determinations: (1) spirit, (2) rosin, (3) water, (4) solid impurities. Oleo-resins collected on the ground by the *au crot* method contained solid impurities, shavings, sand, etc. Hugues' turpentine is chiefly sophisticated by water to increase the bulk. [By Hugues' turpentine is meant the oleo-resin collected by the French cup and gutter system of which Hugues was the inventor.] Tepid water mixes well with the oleo-resin by energetic stirring. Unscrupulous collectors profit by the fact. When the barrels have come a long way the excess of water renders the resin fluid, and when "dumped" into the store vats of the factory it falls with a peculiar choppy sound, by which the fraud can be detected. But if the oleo-resin has only come a short journey, and without shaking or jolting, the fraud is difficult to detect. Fraudulently added water may be detected by plunging the naked arm or a piece of polished or smooth wood into the oleo-resin. If the oleo-resin adheres but little to the arm or to the wood, water has been added thereto. But this rule of thumb test gives no idea of the extent of the adulteration, and may occasion errors of over 5 per cent. A systematic examination of the crude turpentine oleo-resin is difficult;

the whole mass cannot be tested and the difficulty in obtaining a fair average sample will be at once perceived. This difficulty is not, however, insurmountable, and ought not to stand in the way of the moral and material advantages which the turpentine trade has the right to expect from the chemical control of the raw material. By taking two or three samples by a long-handled dipper from each barrel as its contents are being "dumped" into the factory tanks a fair average sample representing the bulk may be obtained. The oleo-resin may also be sampled in the barrels by inserting through the wide bung-hole of the barrels a sort of cheese-taster drill, consisting of a tube 4 in. in diameter and capable of being closed at the lower end by means of a turning-plate riveted on a tringle rod rising up to the top of the drill.

Storing the Oleo-Resin at the Turpentine Distillery.—In fine weather the barrels of oleo-resin are sometimes emptied directly into the stills. More often the oleo-resin is stored in tanks, 3 feet deep, placed 50 to 80 feet from the factory, built of ashlar or made of bricks, covered with tiles and fitted with iron doors, all to provide against fire. The bottom is made of puddled clay, on which is a layer of concrete, covered by a coat of cement, or by tiles. The whole inside surface is then coated with rosin oil. Over the top of the tanks are cross pieces on to which the barrels to be discharged are rolled.

Charging the Turpentine Stills with Oleo-Resin.—The oleo-resin is shovelled from the tanks into trucks, in which it is run to the stills. In winter the oleo-resin hardens and is detached by a shovel reddened in the fire, a dangerous practice which may cause fire. In any case, it darkens the oleo-resin and induces evaporation of the spirit, already diminished (1) by exposure on the "quarres," (2) in the collecting cups, (3) in the factory storage tanks. The latter should be closed with only sufficient ventilation to keep them fresh.

Estimation of Water and Impurities.—About 100 c.c. (say 92 grammes) are weighed into a flask, 92 c.c. turps added, and the whole heated on the water-bath. The fluid mass is run through a flannel filter which retains solid impurities which are washed with spirits of turpentine and weighed. The filtrate separates rapidly into two layers, (1) a varnish floating on the top of (2) a layer of water which is measured in a graduated test-glass on foot. Separation is rapid, with 1½ c.c. of turps for every gramme of oleo-resin to be tested.

Direct Estimation of Spirits of Turpentine.—The most accurate method is by expelling the spirits of turpentine by gradual heating to its boiling-point, 156° C. (312° to 318° F.) and to aid rapid expulsion by injection of a current of steam. By dry distillation almost constant results are obtained provided the temperature be watched and the natural water in the oleo-resin utilized. The soft resin is run into a glass flask fitted (1) with a thermometer graduated from 50° to 200° C. (122° to 392° F.), (2) a bent tube connected with (3) a condenser. The flask is heated on a sand-bath. Both water and

spirit almost all pass over between 95° to 100° C. (203° to 212° F.). To get the last trace over the thermometer is allowed to rise to 150° to 156° C. (302° to 318°·4 F.), carefully watching the heat so as to avoid bumping between 110° C. and 130° C. (230° to 302° F.). The spirits and water are thus measured. The residue of rosin and solid impurities is weighed, filtered, and the increase in weight of the filter washed with turps, or better, benzene gives the percentage of solid impurities. By this direct method there is always a risk of overheating which may partially transform the rosin into rosin spirit which may pass over in the distillate along with the turps.

Gabriel Col's Tests.—The volatile bodies are expelled (1) by heating with steam, (2) by carrying over the turps by injecting a current of steam. The apparatus, all in bronze, includes (1) a jacketed cylinder slightly inclined on its support to aid the exit of the rosin. Steam circulates in the circular jacket 1½ inch wide. (2) A V steampipe opening in one of the bottoms heats the interior cylinder; (3) a perforated pipe for steam injection into mass to be distilled; (4) a charging hopper ending in the inside cylinder which can be closed by a joint of sheet asbestos tightened by a strap screw; (5) a door or sluice for discharging the rosin; (6) a pipe and continuation with dome for carrying off steam and turps and for the return to the cylinder of the most volatile portions; (7) a coil condenser; (8) a metal pressure gauge; (9) an expansion vessel for steam of heating coils closed by valve or automatic joint. *Process.*—The apparatus is heated by steam in the circular jacket only; the steam is then turned off, and a given weight of the oleo-resin to be tested, say 800 to 1000 grammes, is introduced, the hopper closed, steam, 1 kilo per sq. cm., again turned on to the jacket, and the valve at the exit of the expansion vessel is regulated so as only to evacuate condensed water. The flow from the mouth of the coil is kept up by bringing the pressure gradually to 3, 4, 5 atmospheres. At about 4 atmospheres the water in the oleo-resin is completely driven over a point, which may be ascertained by examining the condensed liquid. The water is collected and weighed Between 4 to 5 kilogrammes per sq. cm. of pressure the injection of water is commenced and gradually increased by means of an entrance valve carrying a movable index in front of a graduated circle. When the water from the condenser shows no more globules of spirit the test is finished. The injection is stopped and the rosin heated for a minute before being evacuated through the sluice door on to a wire-gauze filter. Finally the apparatus is cleaned of traces of solid matter by further injection of water into the interior of the cylinder. Each test lasts 15 to 20 minutes and gives the percentage of (1) spirits, (2) water, (3) rosin, and (4) solid matter in the crude oleo-resin. Much useful information is got by the manufacturer testing his deliveries. Such tests afford a substantial basis for purchasing contracts. Again, besides throwing light on the process to be followed in manufacture, a previous test enables the final results to be anticipated, but there are difficulties in the way of buying according

to the percentage of spirits of turpentine and rosin and on the market value of these two products. At the outset it is necessary to inquire into the nature and extent of the sophistication and frauds to which the oleo-resin is subject. Some of these lie to the charge of the distiller himself who supplies the collectors with casks of greater capacity than their face value. The unit adopted in France is the chalosse barrel, supposed to be of 340 litres, about 75 gallons capacity. But the actual capacity of the casks lent is said to be 346 to 348 litres, say 76 to 76½ gallons, and sometimes 350 to 355 litres, say 77 to 78 gallons. Sale by weight would give a solid foundation to the trade and would assure the collector of evident good faith, and the distiller then would have more power to suppress the numerous frauds on the part of the seller, such as barrels not completely filled, barrels closed by too big a plug of moss retaining 1 to 4 lb. of oleo-resin, addition of about 5 per cent of cold water or of about 5 to 10 per cent of hot water, of white clay to increase the cohesion of the water-logged oleo-resin, of sand and shavings, or the withdrawal of a portion of the spirits by continuous evaporation. The proprietor and the collector have each an individual interest in delivering the largest quantity of crude product in virtue of the payment in kind lease in force between them.

The yield of spirit or essential oil depends on the season during which the oleo-resin is exuded, the age of the pine, the soil in which it grows, the solar heat, the aspect of the forest and its general surroundings, etc. The old pines of the dunes yield an oleo-resin which hardly contains more than 35 kilogrammes (say 77 lb.) of water per barrel, whilst the young pines of the small wastes yield sometimes more than 45 to 48 kilogrammes (99 to 106 lb.). The following were figures given by a Landaise distiller. If, for instance, we fix the gross profit to the turpentine distiller at 15 per cent, we can easily get the price of the resin from its composition, e.g. take an oleo-resin yielding 20 per cent of spirit and 70 per cent of rosin. The spirit being quoted 56 francs and the rosin 12 francs per 100 kilogrammes, the price of the resin delivered at the factory could be calculated thus:—

	Francs.
20 kilogrammes of spirit of turpentine at ·56 francs	11·2
70 kilogrammes of rosin at ·12 francs	8·4
Gross value of 100 kilogrammes of oleo-resin	19·6
Deduct 15 per cent on 19·6 francs	2·94
Net value of 100 kilogrammes of oleo-resin	16·66

Purification of Turpentine Oleo-Resin: Open Pan Method.—The purification of the crude oleo-resin includes (1) melting; (2) clarification; (3) decantation and straining. (1) *Melting.*—The oleo-resin is melted in open, cylindrical, copper pans, 6½ feet wide, 20 inches deep, with a slightly concave bottom, with a 4-inch perch. They contain about 330 gallons. The pan is filled from a truck or barrow, and

heat is applied, very gently, as in melting tallow, whilst a workman stirs the mass, continually, so as to distribute the heat uniformly. The temperature should not exceed 90° to 100° C. (194° to 212° F.), and the heat is stopped, directly it begins to boil, as soon, in fact, as the shavings, hitherto swimming about, are carried to the sides of the pan by the current of liquid. (2) *Clarification.*—To clarify the mass, the fire is quickly withdrawn. Some even throw water on the fire and on the bottom of the pan. If this rather difficult operation be successful, the fluid mass separates, in four or five hours, into several layers, shavings and bark on the top, a layer of oleo-resin underneath, and coloured water on the bottom, along with a deposit of earth and sand. (3) *Decantation and Straining.*—The shavings and bark may be separated by passing the oleo-resin through a straw screen, or, better, through a wire-gauze sieve. The oleo-resin is run out, through holes at different levels, or through a movable pipe, with a square elbow inside the pan. The pan usually has no orifice, and is emptied gradually by a dipper. The sand and dirt are run on to a sieve placed above a tank. In this tank there slowly forms a lower layer of coloured water, and a layer of inferior grade oleo-resin. Pitch and tar are recovered from the residual, resinous sand and dirt. In a factory with a still of the capacity of one barrel, making ten distillations a day, it is better to use two preparatory pans of five barrels than one of ten barrels capacity. With small pans the heating surface increases, the boiling is done quicker, and the mass deposits more rapidly. One pan, therefore, is prepared on the previous evening for next morning's work, and the second pan is got ready between two and three o'clock in the morning for the afternoon's work.

Purification of Turpentine Oleo-Resin: Close Pan Method.—To avoid loss of spirits of turpentine by the evaporation incidental to open pans (2 to 3 per cent), *Dromart*, in 1857, designed a close pan, fitted with an agitator and movable trap-doors, allowing the introduction of oleo-resin without moving the lid. The trap is opened by manipulating a lever to allow the oleo-resin contained in the feed vessel to fall into the pan. A circular gutter, filled with water, makes a hermetic joint with the lid, which is provided with a rim filled with cold water. Two workmen stir the mass by working another lever. After three to four hours a thermometer indicates 85° to 90° C., and when tested through a trial hole in the lid a jet of steam blows out. The fire is put out, the melted mass cooled by adding through the trap one or two boxes of oleo-resin. The stirring is quickened, after which it is allowed to stand for twelve hours and decanted to a certain depth from the bottom through pipes for the purpose. When the oleo-resin is too poor in turps to settle out well, it is mixed in a hermetically sealed jacketed pan with 6 per cent turps. Spent steam is injected into the jacket at 80° to 100° C. and the vapour disengaged condensed. The hot paste is run into large decantation vats fitted with lids with hydraulic seals and connected with a condenser. Three

layers form after twenty-four hours: (1) A muddy deposit of organic and mineral matter. (2) A middle layer of brown water. (3) An upper layer of turpentine oleo-resin fluid, enough to be strained and so freed from wood particles. But, instead of diluting the oleo-resin with spirits of turpentine to bring it to a normal density, Dalbouze, a constructing engineer of Dax, proceeds in an inverse manner. He increases the density of the water by adding soda crystals. His pan is a Dromart's pan heated by a steam jacket and a steam coil. The mixing is done by an agitator with a vertical axis driven by a pulley. After fusion and clarification the lid with the hydraulic joint is raised, the mass skimmed, and the purified oleo-resin decanted into a close vessel. Lapeyrere simply eliminates solids. The water thus remains after straining mixed with the oleo-resin. The turpentine oleo-resin

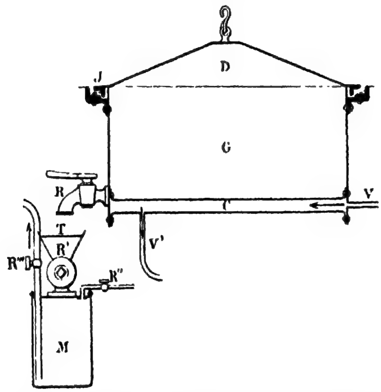


FIG. 9.—Dorian's pan. G, pan for heating crude oleo-resin; D, lid raised by pulley; J, hydraulic joint; C, steam jacket; V V', steam; T, sieve; M, montejus; R R' R'' R''', taps.

is crushed between rolls heated with tepid water. The oleo-resin is melted in two wrought-iron pans by a steam coil connected with a pipe fitted with a sluice valve. The second pan has a wire-gauze sieve cleaned by an agitator with horizontal blades. The melted mass is run into a third pan with three fine sieves from which it passes to the stills. Dorian Brothers, Junior, make a melting pan (Fig. 9) of steel plate, 7 feet 6 inches with 40 inches of useful height. The lower part has a double bottom with a space C of about $2\frac{1}{3}$ inches between the two through which steam is led from V. It is closed on the top by a lid D with a hydraulic joint J which guarantees liquefaction in a closed vessel. The melted oleo-resin is simply strained in T and fed into the still by a montejus M actuated by steam pressure. It is a closed cylinder of the capacity of one barrel, fitted with two pipes R'' R''', the one of 0·07 metre ($2\frac{3}{4}$ inches) in diameter R''' intended for lifting the oleo-resin and reaching to the bottom of the cylinder, and the other R'' fixed on the top of the

receiver and leading to the escape steam. The raising of the oleo-resin is so rapid that three seconds suffice to run the 340 litres in the cylinder into the still. In *Dorian's* process, as well as in *Lapeyrere's*, the turpentine oleo-resin retains the adventitious water present in the resin. The elimination of this water can, moreover, be dispensed with, since water is injected into the resin during distillation. In the preceding processes everything is melted; the most fusible portions are thus superheated, hence great increase of fuel expenditure, loss of spirits, and blackening of the rosin. *Lartigau* avoids agitation, allows the heavy portions to descend, and decants the light portions as they melt. He uses two superimposed jacketed pans fitted with steam coils. The light particles are decanted from No. 1 through a constantly cleaned sieve. In No. 2 the solution of the lumps which the fluid portions have been unable to dissolve is completed.

Turpentine in Paste Form. "Artificial" Venice Turpentine (p. 59).—The turpentine oleo-resin obtained as described is sometimes used in industry as turpentine paste after dissolving it in rosin oil; 1400 lb. of turpentine oleo-resin are mixed with two petroleum casks of 180 kilogrammes (396 lb.) of *blonde rosin oil* from the middle runnings. Heat is applied very gently for two hours, the heat being withdrawn before boiling, as soon in fact as the mass is warm. If overheated the liquid primes like milk and runs over. Paste turpentine may be obtained by exposing the resin to the solar rays. Fusion then only occurs slowly but superficially. Turpentine paste is used in the making of varnish, paints, and sealing-wax. The total quantity made is unimportant and is possibly marketed as Venice turpentine.

French Methods of Distilling Crude Turpentine Oleo-Resin (*a*) *over a Naked Fire.*—The objects of the distillation of crude or purified turpentine oleo-resin are: A. The separation by heat and condensation of the water and essential oil, liquids which in virtue of (1) their insolubility in each other and (2) of the differences in their densities rapidly separate into two superimposed layers. B. The production of a residual product well freed from water, filtered on its discharge from the still, and yielding rosin of different grades according to its depth of colour.

TABLE XVII.—CLASSIFICATION OF THE DIFFERENT METHODS OF DISTILLING TURPENTINE OLEO-RESIN.

Substances distilled	Crude turpentine Pure turpentine	Distillation of crude oleo-resin After purification
Heating by	Wood or coal By steam	By naked fire By steam
Water added to the distilling mass as	Liquid water Liquid water and steam Steam alone	By injection of water By mixed injection By steam injection
Pressure in still	Atmospheric pressure Partial vacuum	Under normal pressure Under reduced pressure

Stills working under reduced pressure require complicated vacuum plant and perfect tightness which renders their use hardly economical. Almost all the stills, therefore, have their exits in the air, and the pressure to balance is 760 millimetres. Now according to a well-known physical law, a liquid boils when the tension of its vapour equals or overcomes the atmospheric pressure which it supports. If spirits of turpentine be distilled alone it boils at a temperature of 156° C. (312·8° F.), a temperature at which the vapour of the essential oil equals the atmospheric pressure. Pure spirits of turpentine boils at 156° C., but the commercial oil at 159° C. (318·2° F.). If water be heated by itself alone, it is at the moment when it has reached 100° C. (212° F.) that the vapour disengaged possesses a tension capable of balancing the atmospheric pressure. But if a mixture of spirits of turpentine and water be heated at any given temperature, the individual tensions of the two vapours combine, and the total tension of 760 millimetres is reached at less than 156° C. (312·8° F.), and even at less than 100° C. (212° F.), (Dalton's law). The following results on the tensions of (*a*) steam and (*b*) of steam and the vapour of spirits of turpentine are due to Regnault. The third column of tensions is deduced from Dalton's law, by adding together the individual tensions corresponding to spirits of turpentine and water.

TABLE XVIII.—TENSION (*a*) OF STEAM, (*b*) OF SPIRITS OF TURPENTINE, (*c*) OF SPIRITS OF TURPENTINE PLUS STEAM.

Temperature.	Steam.	Spirits of Turpentine.	Mixture of Turpentine Water.
0°	0·46	0·20	0·66
90°	52·54	9·10	61·64
100°	76·00	13·10	89·10
140°	270·70	46·40	318·10
150°	353·10	60·50	413·60
159·2°	—	76·0	—

This table shows that from 90° to 100° C. (194° to 212° F.) the tension of the vapours from the mixture of spirits of turpentine and water increases from 61 to 89 centimetres. There thus exists, between 90° to 100° C. (194° to 212° F.), a temperature in regard to which the tension of the mixed vapours is 76 centimetres. This temperature as found in actual practice is about 95° C. (203° F.). So, in distilling pure turpentine oleo-resin, the essential oil distils at 156° C. (312·8° F.), but by adding water the spirit distils about 95° C. (203° F.). The injection of water therefore has a double advantage, as it lessens the fuel expenses and obviates the high temperatures which darken the rosin. If too little water be used, the temperature rises; if too much, the fuel expenses increase. The temperature rises, moreover, as the proportion of oil in the still diminishes. When the distillate ceases, the rosin must be heated to a temperature a little above 159° C. (318·2° F.) in order (1) to drive over the last traces of

essential oil, which otherwise would leave the rosin rather viscous; (2) to run off the injected water, which would give the rosin an opaque appearance. Besides water the still contains dry products, which boil at 220° C. (428° F.), the tension of the vapour of which can be neglected at the temperature at which the mixture of turps and water distils. The vapour tensions in Table XVIII may be represented graphically; each point of the curve of the tensions of turps

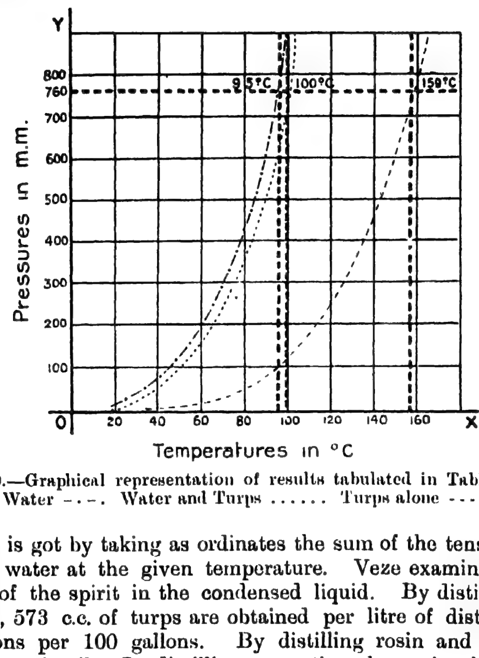


FIG. 10.—Graphical representation of results tabulated in Table XVIII. Water - · - . Water and Turps . . . . . . Turps alone - - - -

and water is got by taking as ordinates the sum of the tension of the turps and water at the given temperature. Veze examined the distribution of the spirit in the condensed liquid. By distilling turps and water, 573 c.c. of turps are obtained per litre of distillate, say 57·3 gallons per 100 gallons. By distilling rosin and water the yield of turps is nil. In distilling turpentine oleo-resin the yield in turps constantly decreases between the limits given.

TABLE XIX.—FRACTIONAL DISTILLATION OF 100 C.C. OF A MIXTURE OF 50 C.C. TURPENTINE OLEO-RESIN AND 50 C.C. OF WATER.

Fractions.	Temperature of the Vapours. ° C.	Turps in gallons per 100 gallons of Distillate.
10 c.c.	97	46·3
20 c.c.	97·5	40·0
30 c.c.	98	35·0
40 c.c.	98·5	29·0
50 c.c.	99·0	18·0

The Still.—The Landaise naked fire still includes (1) feeder, (2) body of still, (3) still-head, (4) condenser. The feeder (1) is capable of holding a still charge of oléo-resin boiled or machined. The oleo-resin is melted in the feeder by a return flame which can be passed at will underneath it. Loss by evaporation is prevented by a hermetic trap. The melted oleo-resin runs into body of still through a pipe with tap. The body of still consists of three copper pieces: (1) a flat bottom, slightly bomb-shaped towards the interior, 10 to 15 mm. thick, fitted with a high collar; (2) body of still riveted to bottom 3 to 4 mm. thick; (3) crown riveted to body of still fitted with a joint in the form of a gutter in which the still-head rests. The body of the still has two orifices: (1) the feed pipe which descends to within 16 inches of the bottom; (2) the pipe for discharging the rosin placed on a level with the bottom and closed by a wooden plug held in a handle. The body of the still is in the form of a truncated cone 40 inches deep, 40 inches in diameter at the base, and 30 inches in diameter at the top. It holds 66 to 88 gallons, and the charge is 55 to 66 gallons. The still-heads are either dome-shaped or flat. The flat form facilitates the exit of the vapours. The still-head rests on two joints, one on the top of the body of the still, the other at the top of the serpentine condenser. On the upper part of the still-head a copper vessel is fixed, fitted with a tap discharging into the still. The slope of the lower face of the still is 1 in 20. The serpentine condenser consists of five or six superimposed spirals round a circle 6½ feet in diameter. This coil is placed in a vat of cold water; its length is about 130 feet, its diameter 8 inches at the entrance, diminishing gradually and imperceptibly to 2 inches at the exit. The condensing surface equals 11 to 12 square metres. The distillate runs into a tank, where the water and turps separate. The latter has a strong resinous taste and must be led far from dwellings to prevent well pollution. Knowing (1) the temperature of the vapours emitted, (2) the temperature and weight of the liquid distillate, turps, water, rosin, and the heat absorbed, the amount of cooling water to supply can be calculated. But it is necessary to bring into the calculation the specific heats of rosin (0·46), of spirits of turpentine (0·47), and of water (1·0), as well as the heat of vaporization of spirits of turpentine, 69 calories, and of water, 437 calories. Dromart in this way calculated that for a vat containing 6000 litres of water at 10° C. the quantity of water to supply is about 400 litres per still charge of 250 litres of turpentine. Practically this figure, he says, appears a little low if the condensed liquid is not to exceed 20° C. (68° F.). The pipe for leading in the water must always open in the bottom of the vat, and the taps are so regulated that the quantity of water which runs in equals that which runs away. For this a second vat or reservoir into which the water is pumped is necessary so as to be able to regulate the entrance of the water into the condenser. The quantity of water may also be regulated by maintaining the temperature of the condensed liquid at about 20° C. (68° F.), and the temperature of

the water running away at about 70° C. (158° F.). The condensation of the vapour seems to be complete after the first convolution of the coil, and the succeeding spirals simply cool the liquid. The calculation, however, shows a consumption of 40 kilogrammes (88 lb.) of dry wood per charge, the kilogramme producing 3000 calories, of which 1500 are utilized. This useful heating effect fails (1) on account of the bad plan of the furnace, (2) because of the small extent of heating surface in proportion to the weight of matter to be vaporized. The body of the still is hardly heated except on the bottom, the flues arranged round the calandria quickly corrode the metal and are of but little use. If the capacity of the still be doubled so as to bring it to 680 litres (150 gallons) the heating surface per 100 kilogrammes of substance is still further decreased and is insufficient for the easy cleansing of the still from rosin by injection. The body of the still, moreover, is completely enveloped in masonry and preserves a heat which prevents the condensation of the spirits before it passes into the still-head. The masonry work includes a furnace closed by two doors, the one for stoking, the other for removing ashes. The furnace is 1 metre in height (3·28 feet) by 1 metre in length. The grate is half-way up and in front. The useful surface is ½ square metre. The flame impinges on the bottom of the still and the gas escapes by two flues, a bifurcated one either passing or not under the feeder, the other passing under a pan where water may be boiled for making yellow rosin. Some distillers have tried to substitute coal for wood as fuel. Here are some results got in 1901 in a Bordeaux-Brienne factory :—

	Francs.
50 bundles of wood at 0·35 franc each	17·5
45 kilogrammes of coal at 3 francs per 100 kilogrammes .	13·5
Daily difference for 14 barrels	4·0

With good wood the difference decreases, and the two methods are about equal in economy. From the point where the products begin to flow from the condenser the distillation comprises the following phases :—

1. Before Injection	Incondensable gases issuing as white fumes. Water only. Water and green spirit, first runnings. " colourless spirit. Colourless spirit only.
2. During Injection	Water spirit and middle runnings. Water and yellow spirit, last runnings. Injection water only.
3. After Injection	Disappearance of condensed products. Cooking of the rosin.

The rosin from one charge is run off, the liquefied oleo-resin in feeder is run into still and fire urged. The heat being uniform throughout the mass the first portions distil green from copper salts on still sides. Water and colourless turps then distil. By and by the water decreases, then spirit alone flows in small jet.

At this point the mass is boiling and making a dry, harsh noise. As soon as the flow of water has ceased and tumultuous boiling makes itself heard, the workman injects tepid water into the pan taken from the top of the condenser vat. As soon as injection is begun the fire is urged. The intensity of firing and the quantity of water injected should always be reciprocally regulated. If the temperature rise too high the noise of boiling is louder, the relative amount of water in the distillate diminishes, and the distilled spirit is red. If too long a delay occur in increasing the injection, when the water is forced in, a considerable amount of steam is disengaged, which not being able to effect a quick enough passage through the still-head escapes through the joints.

If the temperature be too low the injection water is only partially vaporized, and the excess produces globules which break up and cause explosions which are, sometimes, but rarely, so violent as to blow off the still-head. But low temperature distillation is slow, and the mass sometimes froths and primes. Towards the end yellow spirit distils, then water alone. The spirits from the first and last runnings are collected together (but apart from the middle runnings) in an earthen jar. They may be rectified, but generally they are added to the next charge of the still. The spirit from the middle runnings is milky. It clarifies naturally after a few days' standing in the tanks, when it is stored in cylindrical vessels of wrought copper protected from light. When water alone distils injection is stopped. The still-head is removed by a pulley or by hand and the rosin run out through the bottom pipes. Each charge takes 60 to 80 minutes. Injection begins after 15 to 20 minutes, and it takes 50 to 60 litres of water for 340 litres of oleo-resin (say 5 to 6 gallons per 34 gallons), producing 60 to 75 kilogrammes of spirit (60 to 75 lb. per 34 gallons). So as to work more rationally Dromart uses a pyrometer in the body of the still. Ordinary thermometers would soon be broken by the sudden rise from 40° C to 140° C. They may, however, be protected by a copper sheath. Dromart's pyrometer consists of an iron tube fitted to a cast-iron cell filled with mercury and dipping into the oleo-resin which is being distilled. The mercury supports a float fixed to a steel rod inside the iron tube. The top part of the rod moves a mobile lever in front of a graduated arc. The weight of mercury to place in the cell is determined by boiling water in the body of the still and adding mercury until the needle of the dial is at 100. In distilling with the pyrometer the water contained in the oleo-resin is first distilled off, then injection is started at 135° C. The heating and injection are so regulated as to keep the temperature between 135° and 160° C. If pyrometers do not get into immediate equilibrium with the temperature of the substance being distilled, and if they give no warning of tumultuous boiling, yet they are useful, and every oleo-resin distiller should use one as a guide to the progress of the distillation. A second guide is the proportion of water in the distillate, which ought not to vary much whilst the middle runnings are being distilled. A third guide is the noise of the still during

boiling, easily heard by placing the ear on the handle of the plug which closes the round discharge pipe. *Sluices.*—The tap placed between the feeder and the body of the still involves a gap in the masonry, and to discharge the feeder rapidly the pipe must have a great slope and the tap a wide mouth. The tap is therefore in many distilleries replaced by a sluice wrought by a lever. At the end of the distillation the still-head must be lifted off so as to let the rosin run out at atmospheric pressure. This may be obviated by fitting to the still-head a pipe with a valve which is opened to let in the air. This pipe is also very useful to follow the noise made by the boiling mass. The condensing surface is increased by placing the descending pipe from the still-head in a semi-cylinder traversed by a current of water. The serpentine sometimes bifurcates 8 inches from the top to re-unite near the orifice. A tap is fixed on the pipe (which conducts the water to be fed into the still) 8 inches above the funnel so as to regulate the water injected into the still. The heat required to vaporize this water removes much caloric from the resinous mass, the fire must therefore be urged and then the excess of heat diminished by injecting more water. This entails delay and irregular working in distillation, drawbacks obviated by a steam jet from a perforated pipe spreading the steam over the bottom of the still. If it be purified oleo-resin that is being distilled injection is begun sooner than with crude oleo-resin. After about 10 minutes steam injection is regulated by a valve within easy reach of the distiller. If the temperature be too high water is injected along with the steam, but generally water is only injected at the end of the operation so as to dry the rosin by the greater heat. Excellent results are thus obtained. The heat keeps under, the rosin is pale, the operation is shorter, 40 to 50 minutes. A well-distilled charge takes 50 kilos (20 water, 30 steam). When rosin is low in price the crude oleo-resin is mostly distilled with water.

(*b*) *Steam Distillation of Spirits of Turpentine.*—If the greatest care be not taken in the naked fire distillation of the oleo-resin the temperature of the resinous mass rises to 180° to 200° C. with the following bad effects: the woody fibre in crude oleo-resin is charred and the rosin, already darkened by the overheating, still further discoloured, whilst a portion of the rosin is distilled over as rosin spirit and rosin oil, lowering the value of the spirits of turpentine. Naked fire distillation is difficult to regulate, and only somewhat small quantities can be distilled at a time. Fire risks are numerous. These drawbacks are obviated by steam distillation, but even that method itself is not perfect. The plant is dear, redemption and depreciation heavy, and a big supply of raw material not always to be had owing to bad means of transit, and the greater number of steam-distilling plants involve previous purification of the resin. Again, the additional commercial value is small and little economy of fuel is effected. The rosin is difficult to dry. But if an ample supply of oleo-resin and fuel be available, steam distillation yields purer and finer spirits than over a naked fire, the rosin is not overheated and the distillation is

simple and easily regulated, requiring no special training and there is less risk of fire. Purification and distillation of 3 metric tons (6600 lb.) of oleo-resin requires 860,000 calories, obtained from 1300 kilogrammes of saturated steam at 160° C. drawn from a boiler of 9 square metres of heating surface and producing 11 kilogrammes of steam per square metre in 12 hours. One kilogramme of pine wood yields 2¼ kilogrammes of steam at 6 atmospheres. By the steam process alone 580 kilogrammes (1276 lb.) of wood are used for 3 metric tons (6600 lb.) of oleo-resin, whilst in naked fire distillation 600 to 700 kilogrammes (1320 to 1540 lb.) are burnt for the same amount of oleo-resin. There is little economy in wood fuel, but the economy is greater with coal. Dorian's distilling plant consumes 12 francs (say 10s.) worth of wood for 15 barrels of oleo-resin.

With a well-regulated temperature naked fire distillation may yield rosins quite as transparent and pale as steam distillation produces. The oleo-resin is coloured beforehand, and the heat of the still under normal conditions has no effect. Without a pyrometer the temperature sometimes reaches 200° C. (392° F.), and then the rosin is burnt. But this is due to carelessness and not to the method of distillation. Henry Violette, one of the pioneers of steam distillation, says steam at 100° C. (212° F.) passing through spirits of turpentine brings the latter in its train. Steam heated to 100°, 200°, 300° C. entrains a proportion of spirit which varies but little in each instance and which is at a maximum in the case of 150 parts of spirit by volume per 100 parts of steam. Saturated steam at 3 atmospheres, or even steam superheated to 150 to 200° C., completely deprives turpentine oleo-resin of the 18 to 20 per cent of spirits which it contains. With steam the spirits is limpid like the purest water and gives the highest yield. The rosin is whitish like wax. If this yellow oleo-resin be deprived of its water either by careful evaporation or, better, by passing a current of superheated steam through the mass heated to 200° (392° F.), a dry, very pale, limpid rosin is obtained. Violette estimates that 100 kilogrammes (2 cwt.) of steam are required to distil 100 kilogrammes (2 cwt.) of raw material, a hectolitre (22 gals.) of cold water at 10° C. to condense the mixture of water and spirit from 100 kilogrammes of crude resin, and a condensing surface of 0·05 metre per cubic metre (metric ton) of cold water to be furnished during the distillation. Col says the expense of steam distillation per 1000 kilogrammes (metric ton of 2200 lb.) of crude resin is distributed thus:—

TABLE XX.—COST OF RECOVERING SPIRITS OF TURPENTINE FROM 1 TON (METRIC) OF OLEO-RESIN.

Expenditure on	Francs.	s.	d.
Labour	3·25	2	3·2
Fuel	3·25	2	3·2
Packing and storage of dry products	5·00	4	0·0
General expenses	2·00	1	7·2
Total (9 per cent on purchase price)	13·50	10	3·6

Steam factories are advisable for large quantities of oleo-resin, but for small works, disseminated in the forests and only working 2000 barrels annually, naked fire distillation, with mixed injection, is most advantageous. Moreover, steam factories have not increased during the last ten years.

(b^1) *Distillation of Purified Oleo-Resin.*—Violette installed, about 1860, at the Hume factory, near Bordeaux, two sets of steam distillation plant, one for the *purified*, the other for the *crude* resin. The resin is purified by the ordinary naked fire process, then it is led into a copper cylinder, surrounded by an insulating cover of ashes, contained in a wooden vat. The cylinder (Fig. 11) has (1) a manhole *c* for feeding it with oleo-resin; (2) a rosin discharge pipe *d*; (3) an injection

FIG. 11.—Violette's steam-heated still for distilling purified turpentine oleo-resin.

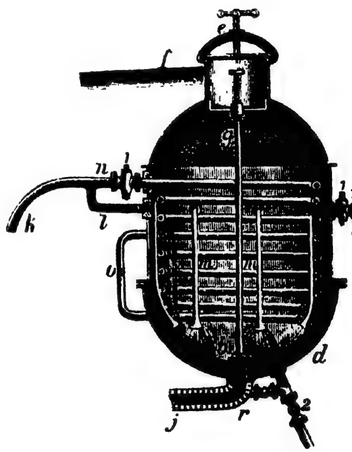


FIG. 12.—Violette's turpentine oleo-resin still (steam-heated).

apparatus of eight pipes; (4) an exit pipe for the vapours *e*. The cylinder holds 6 cubic metres and is charged with 4000 kilogrammes (4 metric tons) of purified resin. When the distillate contains no more spirit, superheated steam 150 to 200° C. (302 to 392° F.) is run into dry the rosin. If the residue be slightly opaque, it must be transformed into yellow rosin, by agitating it briskly with water. The superheater is really a reverberatory furnace on the sole of which are laid four pipes, 4 metres in length. The joints are repaired through gaps. The hearth is lateral, and a very moderate covered fire, the expense of which is insignificant, keeps the steam at 150 to 200° C. (302-392° F.).

(b^2) *Distillation of the Crude Oleo-Resin.*—To work by steam alone Violette dispenses with purification, and introduces the oleo-resin directly into an egg-shaped vessel (Fig. 12). The inferior cupola body

of the still is jacketed and is fed with exhaust steam. The crude oleo-resin, 4000 kilogrammes, say 4 metric tons, is fed in through the door *e*, the vapours escape in *f*, and the rosin is evacuated by the pipe *j*, closed by a plug fixed to the rod *g*. Inside the still are (1) a steam coil for heating fed through *n*; (2) eight steam injection tubes, terminating in a rose, and fed by a pipe *ll*, encircling the still; (3) a pipe leading the steam, taken from the bottom of the coil, into the steam jacket *p*. The condensed water is run off through the tap 2, or by the small coil *r*, placed round the pipe *j*. Before distillation the oleo-resin is melted by circulating heating steam alone. After two hours the mass is melted, steam is injected and distillation starts. After eight hours' flow the operation is finished, and the still only contains rosin, containing a little water which is eliminated by stopping the injection and passing the steam through the coil as long as water issues from the condenser pipe.

Like Violette's factory, Labalaye's at Manco Becquet (Monte de Marsan) with a large still has been wrought by steam for a long time, over forty years. The crude oleo-resin is previously purified by steam; 30 hectolitres (660 gallons) of crude oleo-resin are run into the still No. 1, of 45 hectolitres (990 gallons) capacity, and are heated in the afternoon for an hour and then let stand till morning. The steam given off during this first heating passes through a valve to a condenser, a bell of 2 to 3 hectolitres (44 to 46 gallons) capacity watered from the top. After this partial condensation the vapours are completely liquefied in a long coil in a vat of 300 hectolitres (6600 gallons) capacity. The purified oleo-resin got in the still No. 1 is next morning run into still No. 2, which is heated until the spirit is completely expelled. Steam is injected into still No. 2 only. The steam from the boiler is kept at a pressure of 4 or 5 atmospheres which gives for heating and injection a temperature of 145° to 155° C. (293° to 311° F.). The two stills are heated by coils with return of the steam to the boiler. When distillation goes on in No. 2, No. 1 is isolated by closing a No. 1 valve, and when No. 1 is at work the No. 1 valve is opened and the corresponding No. 2 valve closed. The turpentine residues from No. 1 still yield black rosin, whilst the residue from the distillation of the turpentine oleo-resin itself in No. 2 still yields pale rosin.

Gabriel Col's Turpentine Oleo-Resin Steam Still is cylindrical, ending, top and bottom, in two truncated cones. The small base of the upper cone carries (1) a feeding hopper, holding a whole charge of say 420 kilogrammes (924 lb.); (2) a copper goose-neck connected with a condenser; (3) accessories: steam pipes, safety valve, thermometer, and pressure gauge. The body of the still includes an inner vessel, completely surrounded by a steam jacket of 4·5 kilogrammes of pressure, which ascends round the feeding hopper. The interior of the still contains a steam coil and a rose injector. The lower cone is a trap for discharging the rosin. The still is heated by dry steam only, carefully freed from any condensed water by passing through a sheet-

iron vessel provided with an automatic discharge. The rosin being run out the still is immediately closed, filled with purified resin, melted in the hopper. By opening a trap, carrying an index, moving round a graduated arc, the distiller applies injection steam gradually and the temperature increases regularly during the whole course of the distillation, rising from 82° C. to 153° C. (179·6 to 307·4° F.). At the condenser exit there appears successively (1) incondensable gases; (2) a small quantity of green spirits; (3) pure spirits which may be sold as rectified; then, towards the end of the distillation, (4) yellow spirits. The coloured spirits of the first and last runnings are collected in the same vessel, and are utilized in the purification of the oleo-resin. The distillation takes about forty-two minutes, of which six are preparation, eighteen flow of spirits, and eighteen to extract last traces of volatile products. At the end of the operation the injection is stopped and the resin run into a truck. One set of this plant distils the turps from 7500 kilogrammes (7½ tons) of purified oleo-resin in twelve hours.

Dalbouze's copper steam still is shaped like Col's, a cylinder ending in two cones, heated by a steam jacket up to two-thirds its height. The inner body has numerous vertical steam pipes. The heating steam reaches 5 to 6 atmospheres, 155° C., and a charge takes forty-five minutes to distil.

Garnier Still is a horizontal cylinder, heated by a steam jacket and copper coil. The still is charged with crude oleo-resin softened by a slight heat, or with completely purified oleo-resin. The still, holding 50 kilogrammes of crude oleo-resin, is heated to 158° C. (316·4° F.) with 6 kilogrammes per square centimetre steam. No thermometer is used. Distillation takes one hour and twenty minutes, and injection is regulated by examining the distillate. The gooseneck is prolonged by a condenser containing 150 pipes traversed by a very rapid current which shortens the condenser coil. Towards the end of the operation the communication between the coil and the condenser may be cut, into which cold water is run, whilst the steam is urged up to 160° C. (320° F.). The cold water passing through the tubes condenses the vapours and produces partial vacuum in the still which facilitates the dehydration of the rosin which is discharged on to an oscillating filter.

Dorian's Steam Still is simple, substantial, and gives good results; economizes fuel by returning the condensed water from the heating steam direct to the boiler instead of letting it run away in pure loss or even leading it to the boiler feeding tanks. It consists of (1) a steam boiler; (2) a still; (3) a condenser. The boiler feeds still by pipe on steam dome, not going beyond 6 kilogrammes per square centimetre. The still includes (1) an oleo-resin feed-valve; (2) a rosin discharge valve; (3) the prismatic body of the still; (4) a steam jacket; (5) reheating pipes crossing the body of the still from side to side through which steam passes; (6) a dome; (7) a still-head; (8) a pipe which leads the condensed water from the steam

condensed in the still back to the boiler. This return of the water is effected naturally. The pressure is in fact equal in the boiler and in the steam jacket of the still; the latter being slightly higher the condensed water runs back to the still solely by its own weight. The oleo-resin divided into thin layers by the pipes quickly begins to distil. Water is injected from a rose with tap on the dome. The vapours are condensed by a tubular condenser and with an ordinary coil. The condenser consists of long pipes of 3 to 4 metres riveted on two steel plates. The vapours circulate in the tubes surrounded by a current of cold water. This condenser is so effective that the coil by which it is continued is almost useless. The heating surface amounts to 11 square metres for a still body of 350 litres capacity which enables 340 litres of crude oleo-resin to be distilled in forty minutes. The cost of a steam factory on Dorian's system is much less than by any of the above methods. An installation costing 20,000 francs, say £800, includes: (1) a tubular steam boiler with accessories; (2) a Dorian still of steel plate tested at 10 kilogrammes of 340 litres of useful capacity; (3) a rectilinear condenser, a coil, and a refrigerating vat; (4) a preparatory pan for purifying the resin and a montejus; (5) accessory piping as well as the cost of erection and putting in working order.

Electric Method of Distilling Turpentine.—Pine-wood contains a series of volatile hydrocarbides with boiling-points varying from 130° to 250° C. The mixture which boils between 155° and 170° C. forms what is commercially known as turpentine. The principal constituent of this turpentine is pinene, with a boiling-point of 155° to 156° C. The process of obtaining turpentine from wood by distillation is an extractive one, in that the turpentine exists in the wood, substantially, in the form in which it is obtained, and is not a product of decomposition at the time of extraction. At 175° C. the pinene of the turpentine begins to decompose into a mixture of lighter and heavier hydrocarbides, decomposition being practically complete at 270° C. It is therefore necessary to distil turpentine within relatively narrow temperature limits. If the wood from which the turpentine is distilled is not heated enough part of the turpentine will be left in it. If the temperature is too high part of the turpentine will be destroyed. Many of the products formed in breaking up turpentine have strong odours, and a small percentage materially affects the selling price that the turpentine produced, as the smell nauseates the painter using the turpentine. With ordinary methods of distillation in iron retorts it is very difficult to so regulate the retorts that no overheating of the external part of the charge of wood takes place. It has been known for many years that the fir-wood of the North Pacific coast contains a considerable quantity of turpentine, and efforts have been made to utilize it as a basis for the commercial production of turpentine. The principal difficulties encountered were those inherent in the close regulation of temperature necessary. Some years ago the obvious possibility of close temperature regula-

tion obtainable with heat from electricity suggested the use of heat from electricity in the distillation of turpentine from this fir-wood. At Vancouver, British Columbia, a considerable supply of waste fir-wood was available, in the form of sawmill refuse; the electricity from water-power was also to be had at a low cost. An experimental electric turpentine plant, with a capacity of $\frac{1}{10}$ of a cord, was therefore erected and tested, and subsequently, owing to the favourable report of Dr. Bray, of the Massachusetts Institute of Technology, a commercial plant, with a capacity of three cords per day, was erected and has been in operation at Vancouver since July, 1907.

The wood is filled into oblong "cans," which are wheeled into the distilling shed, picked up by an overhead crane, and dropped into a brick retort, forming one of a group which are placed together to reduce radiation. The upper part of the can forms a flange, which dips into a groove around the top of the retort, filled with tar, forming a gas seal when the gas is in the retort. Electricity at 110 volts pressure is carried through wrought-iron strips threaded through the brickwork on both sides of each retort. The current supply for each retort is controlled by a switchboard of ordinary type, which also holds the direct reading pyrometers, one of which registers the temperature at the outside of the can, and one the temperature at the centre of the can, showing the maximum and minimum temperature conditions. The leads of these pyrometers end in flexible extensions on the top of the retorts, which can be changed from can to can. The turpentine vapour is taken from the retort, through a removable copper outlet pipe. This outlet pipe leads to a condenser which consists of an upright copper pipe, down which a spray of water is passed through the ascending turpentine vapour, and which terminates in a tank at the bottom. The tank serves as a separator for the condensed turpentine and water, the turpentine floating to the top. The excess water from the spray is withdrawn from the bottom of the tank, and the turpentine taken off from the top of the tank into a storage system.

The brickwork of the retort, when a can newly filled with wood is put in, is about 250° C. The cold can rapidly absorbs heat from this brickwork, the temperature of the brickwork being kept up by a current of 400 amperes, which is passed through the resistance strips for about two hours. During this time the temperature at the outside of the can rises from 75° to 130° C., at which turpentine begins to come off and at which time the centre of the can is 45° C. The current is then shut off, and the temperature of the can slowly rises by absorption of heat from the brickwork for two hours longer, when the temperature has reached 150° C. on the outside of the can, and 205° C. in the centre of the can, and the turpentine has been substantially all removed. In practice, it is found that from 90 to 95 per cent of the turpentine in the wood, as determined by analysis, is removed during this interval. While the turpentine is coming off the pitch in the wood melts and runs down to the bottom of the can

and out through perforations, and is collected in the bottom of the retort, from which it is drawn off, at the end of the run, into the barrels in which it is shipped.

It will be noted that the temperature of the interior of the can at the end of the turpentine run is hotter than the outside. This is due to the heat which is beginning to be liberated by the decomposition of the hydrocarbides in the wood. At this point the can is lifted by the overhead crane from the turpentine retort and put into the adjoining retort, a new can of raw wood taking its place in the turpentine retort. In its new position, the original can of wood, from which the turpentine has been extracted, is connected up by another copper outlet pipe to the adjacent condenser. This change of retort and piping keeps the turpentine condenser and piping from being fouled by tar oil or tar products.

Owing to the continued decomposition of the wood, the temperature steadily rises without further use of electricity, and the resulting decomposition gives a product known commercially as "tar oil," and which comes off as vapour and is condensed. The other product of this decomposition is wood tar, which trickles down as the rosin did in the turpentine retort, and is collected in the bottom of the tar retort. In practice it is found that this tar tends to decompose at the final temperature of the tar retort, consequently it is drawn off continuously and during the tar-run, into the barrels in which it is to be shipped. At the end of three hours of the tar-run, the temperature in the centre of the can has risen to 375° C., and tar oil and tar stop coming off. The can is then lifted out and placed on a sand floor, which makes an air seal with the lower edges of the can and protects from combustion the contents of the can, which now consists of charcoal. When the can and its charcoal contents have cooled, which takes about three hours, the perforated bottom is removed and the can lifted, allowing the charcoal to fall out. This is then put in sacks, as required by the trade which consumes it.

Five products are obtained from the wood: (1) turpentine, and (2) rosin in the turpentine retort; (3) tar oil, and (4) tar in the tar retort, and a residue of (5) charcoal. The amount and kind of product derived from any particular supply of wood depend upon its character. The following will indicate the results which are being secured from the British Columbia Coast Fir per 1000 lb. of wood: turpentine, 6·7 gals.; rosin, 168 lb.; tar oil, 5·1 gals.; tar, 68 lb.; charcoal, 323 lb. It may be noted that this charcoal, being retort charcoal and cooled out of contact with air, is tough and suitable for special purposes. The amount of wood held by a can varies with the quality of the wood, but averages at Vancouver about 1000 lb. The electricity used per can is about 90 kilowatt hours, and costs at Vancouver 18 cents per can of wood. The plant is operated by one man on each shift, there being two twelve-hour shifts per day. When the wood is large, an extra man is employed on the day shift to split it.

CHAPTER IX.

TURPENTINE TESTING AND TURPENTINE SUBSTITUTES.

The Three Chief Brands of Spirits of Turpentine.—1. *American* consists essentially of dextro-pinene. The specific gravity is 0·864 to 0·866. Dextro-rotatory, varying greatly from + 8° to + 16°, that of pure dextro-pinene being 21·5°. American turpentine is, when pure, a water-white, limpid liquid with a peculiar and characteristic odour, very distinctive, and readily recognizable. Some samples have a faint straw colour, due to the presence of small quantities of rosin. It begins to boil at 156° to 160° C. (313° to 320° F.), and is completely distilled at 170° C. (338° F.), leaving only a small trace of residue behind. Some poor grades leave a little resinous matter behind, rarely exceeding 2 to 3 per cent. Its affinity for atmospheric oxygen is greater than that of French turpentine. The air oxidation products have a variable rotation, and may be separated into two isomers, the one dextro- and the other levo-rotatory, which by being mixed in equal quantities produce an inactive variety. The spirits of turpentine used for American home consumption would appear to be grossly adulterated with petroleum products by the retailer or middlemen. That exported would, however, appear to be of uniformly good quality. American spirits of turpentine consists of two terpenes, one levo-rotatory, and identical with that which predominates in French spirits of turpentine—levo-pinene; and the other, the chief ingredient, dextro-pinene, which is also found in a state of great purity in *Pinus khasyana*, a tree indigenous to British Burma. (Armstrong).

2. *French Spirits of Turpentine.*—It is levo-rotatory, different samples giving generally − 37°. Its boiling-point is more constant, and its behaviour is altogether more uniform than the American spirit. Terebenthene levo-pinene is, according to Berthelot, obtained from French spirits of turpentine by neutralizing it with carbonate of soda and then distilling *in vacuo*. It is a colourless mobile liquid, boiling at 161° C., with a density equal to 0·864 at 16° C. It is levo-rotatory [$a = -42{\cdot}3°$]. When heated to 250° C. in a sealed tube, it is converted into a mixture of hydrocarbides—the first an isomer isoterebenthene $C_{10}H_{16}$, boiling at 177° C.; and the second, a polymer isoterebenthene $C_{20}H_{32}$, a viscous liquid.

3. *Russian Spirits of Turpentine* is very similar to American. Like the latter it is dextro-rotatory, and varies from + 15° to + 23°,

the deviation of pure sylvestrene being + 19°. Its density also varies from 0·864 to 0·870 (?). It begins to boil about 155° C., the bulk of the distillate passing over between 172° and 176° C., leaving a residue which does not distil below 180° C. It has an unpleasant odour, simultaneously recalling that of Stockholm tar and rosin spirit. Owing to this rank smell neither Russian-Polish nor German spirits of turpentine is in favour with painters, upon whom their effects are greater than that of the American spirit, producing in some individuals headache and great lassitude. Hence its use is not general either as a solvent for varnishes or as a paint vehicle. Kingzett has given the name of camphoric peroxide to the oxidation product of spirits of turpentine. This oxidized product when heated with water is said to yield camphoric acid $C_{10}H_{16}O_4$.

Russian turpentine resembles American turpentine in many of its chemical properties, such as the action of nitric and sulphuric acids; hydrochloric acid gas gives a liquid product, not a crystalline one. Chlorine and bromine act much in the same way. In its degree of solubility it is the same.

Its odour is more marked, especially in the crude grades; these have a brownish tint, but when refined it can be obtained as a water-white, almost inodorous liquid. The specific gravity of the crude is higher owing to impurities and more variable than in the case of American turpentine. The higher range of distilling points distinguishes Russian from American or French spirits of turpentine.

Refining Russian Turpentine on the Small Scale.—Run the Russian turpentine into an untinned steel barrel. Leave space for about 1 gallon of water. Get a 1 lb. tin of caustic soda, costing sixpence, and dissolve it in a pint of water. Run this caustic lye into the barrel containing the turps, screw in the bung, and roll the barrel about on the floor or factory yard for about a quarter of an hour; tilt on end if there be an end bung-hole, let stand over night, and next morning siphon off the purified nice-smelling turps from the dregs; give it a wash with tepid water in another clean wooden barrel, let settle again over night, and siphon it off for use. The soda lye and dregs can be used for making rosinate of soda for drier manufacture, so there need be no loss. This will yield a refined Russian spirits of turpentine equal to, if not superior to, anything on the market.

The oxidation of spirits of turpentine is utilized in oil painting, in which it is used as a vehicle for thinning-out the paint; it is also used as a solvent vehicle for resins in varnish-making. It is said that the greater amount of the oxygen absorbed remains in an available condition, imparting energetic oxidizing properties which facilitate the so-called resinification of linseed oil, i.e. conversion into linoxin. It is, however, more than probable that the resinous acids which oxidized spirits of turpentine leave on evaporation combine with the metallic oxides and carbonates of the pigment to form zinc, lime, lead, etc., resinates which all powerfully contribute to the binding and durability of the film of paint. But when this combination occurs in the paint

keg or tin, the so-called livering of the paint is produced, and that is an objectionable feature.

Tests for Differentiating Different Brands of Spirits of Turpentine and Substitutes.—The following turpentine tests, from an article in "Drugs, Oils, and Paints," may prove useful in qualitative working: In a test tube (size 6 inches by ⅝ inch) place about 10 c.c. of the turpentine to be tested, then add about 10 c.c. of C.P. sulphurous acid (not sulphuric), and shake four or five times until the two liquids are mixed. Set aside for twenty or thirty minutes to allow to separate, then observe the appearance and colour of the two strata.

American Spirits of Turpentine.—Separation takes place very slowly. Upper stratum—Opaque; milky white colour. Lower stratum—Translucent; milky white. Odour—Slight *terpene* smell.

Russian Turpentine.—Quick separation. Upper stratum—Translucent; faint turbidity. Lower stratum—Clear and colourless. Odour—Slight *pungent* smell.

Pine Distillate (Dead Wood).—Medium slow separation. Upper stratum—Opaque; light buff colour. Lower stratum—Translucent; yellow amber colour. Odour—*Distinct tar* smell.

Pine Distillate (Live Wood).—Medium quick separation. Upper stratum—Translucent; lemon yellow colour. Lower stratum—Clear and colourless Odour—*Mild tar* smell.

Rosin Spirit.—Medium slow separation. Upper stratum—Translucent; golden yellow colour. Lower stratum—Translucent; creamy white colour. Odour—*Pungent resin* smell.

Benzine (Petroleum Naphtha).—Quick separation. Upper stratum—Clear and colourless. Lower stratum—Clear and colourless. Odour—*Sulphurous gas* smell.

Solvent Naphtha (Benzol).—Quick separation. Upper stratum—Slight turbidity; faint yellow colour. Lower stratum—Clear and colourless. Odour—*Benzol* and *sulphurous* smell.

Note.—Pine distillate from stumps, dead wood, etc.

The German Pharmacopœia contemplates the detection of adulteration of turpentine with petroleum, by specific gravity, and by means of the solubility of turpentine in 90 per cent spirit. This does not, however, help in the case of the petroleum distillate on the market as a turpentine substitute, with which oil of turpentine is often adulterated. This is best detected with hydrochloric or nitric acid. If the sample is shaken up with its own volume of the acid, and left to separate into two layers, the following appearances are noted. With pure oil of turpentine, the hydrochloric acid layer is turbid, and the upper layer a pale brown. In the presence of as little as 5 per cent of petroleum distillate the acid has a distinct brown colour. With nitric acid the acid layer is clear, of a pale brown, in the case of pure oil of turpentine, the oil taking a pale green tint. In the presence of 5 per cent of petroleum distillate the acid becomes a dark brown.

Effect of Adulteration on the Specific Gravity.—The sophistication

of spirits of turpentine with petroleum spirit is generally done with that fraction which boils at about 155° C. Now the gravity of this distillate is about 0·759; whereas that of recently distilled pure spirits of turpentine is about 0·865. Should a sample show a lower specific gravity than 0·865, the sample is at all events to be regarded with suspicion. Ten per cent of heavy petroleum spirit in a turpentine gives a product which has the same specific gravity as a mixture containing 27·75 per cent of light petroleum spirit.

TABLE XXI.—CHEMICAL AND PHYSICAL PROPERTIES OF SPIRITS OF TURPENTINE AND ITS ADULTERATION (ALLEN).

	Spirits of Turpentine.	Rosin Spirit.	Petroleum Naphtha.	Shale Naphtha.	Coal-Tar Solvent Naphtha.
1. Optical activity	active	usually none	none	none	none
2. Specific gravity	860-872	856-880	700-740	700-750	860-875
3. Boiling-point	156-180	gradual rise	gradual rise	gradual rise	gradual rise
4. Action, in the cold, on coal-tar pitch	readily dissolves	readily dissolves	very slight action	very slight action	readily dissolves
5. Behaviour with absolute phenol at 20° C.	homogeneous mixture	homogeneous mixture	no apparent solution	homogeneous mixture, crystallizing on cooling	homogeneous mixture
6. Behaviour on agitating 3 vols. with 1 vol. of castor oil	homogeneous mixture	homogeneous mixture	two layers of nearly equal volume	like petroleum naphtha	—
7. Bromine absorption dry	200-236	184-203	10-20	60-80	—
8. Behaviour with H_2SO_4	almost entirely polymerized	polymerized	very little action	considerable action	moderate action

TABLE XXII.—COMPARATIVE ACTION OF AMMONIA ON PURE AND SOPHISTICATED SPIRITS OF TURPENTINE (ALLEN).

Pure 0·8678.	Old 0·8693.	+ 10 per cent Rosin Spirit 0·8784.	10 per cent Undistilled Turpentine 0·8784.	10 per cent. Rosin 0·8831.
No effect, mixture separates immediately.	Solidifies in a few seconds, forming a white crystalline mass of the consistency of butter.	An emulsion which becomes clear; the ammonia which separates has a pale yellow colour.	An emulsion which becomes clear on standing. A semi-transparent gelatinous magma of a bluish colour, the liquid above being colourless.	Each drop of ammonia appears to solidify as it falls into the oil. On agitation the whole solidifies into a consistent semi-transparent mass.

TABLE XXIII.—EFFECT OF ADULTERATION ON THE FRACTIONAL DISTILLATION OF 50 C.C. SPIRITS OF TURPENTINE AND SUBSTITUTES.

No. of Sample.	1 1st drop at °C.	2 5 c.c. at °C.	3 10 c.c. at °C	4 20 c.c. at °C.	5 30 c.c. at °C.	6 40 c.c. at °C.	7 45 c.c. at °C.	8 Rosin. Per cent.
1	150	—	158	159	159·5	161	166	1·77
2	156	158	159	160	161	164	170	0·98
3	156	159	159	159	160	162	167	1·41
4	156	159	159	160	161	163	167	0·60
5	157	—	157	158	159	—	165	1·76
6	153	—	157	158	160	—	165	1·01
7	155	157	157	159	161	164	173	—
8	158	163	163	165	166	171	176	—
								Non-vol. Oil at 280°
9	150	176	185	203	252	—	—	24·22
10	125	—	168	175	198	288	—	—
								Rosin.
11	157	180	190	200	210	—	242	1·41
12	154	158	160	161	164	169	183	—
13	154	155	156	156	157	159	161	—
14	152	159	162	168	182	208	235	—
15	258	281	286	300	340	—	—	—
16	155	171	182	202	230	253	288	—
17	60	74	78	86	99	114	130	—
18	91	141	151	156	160	164	171	—
19	75	100	110	123	132	144	152	—

Samples—1-7 American turps; 8 rectified Russian turps; 9-10 rosin spirit; 11 turpentine (rosin spirit); 12 turpentine with 10 per cent rosin spirit; 13 bought as rosin spirit, but similar to turps; 15 "turpenteen" petroleum product; 16 kerosene, 0·810; 17 petrol, 0·702; 18 turps with 10 per cent petrol; 19 coal-tar naphtha, 0·843.

Effect of Adulteration on the Optical Deviation.—The optical deviation of polarized light induced by its passage through any given sample of spirits of turpentine can be determined with sufficient accuracy by the Mitscherlich Half-shadow Polarimeter, using either a 200 mm. or a 100 mm. tube. It consists essentially of two Nicol's prisms, one of which A acts as the analyser, the other P as the polarizer.

Behind the analyser is a small telescope, and behind the polarizer a semicircular plate of quartz which half covers the polarizer. Between these and the analyser lies the operating tube R. The analyser is fitted with a small telescope F. The telescope is focussed on to the quartz plate, and the field of vision appears as a circle divided into two halves as shown in the figure below. A pointer is attached to the analyser, which moves to the right or left on a metal disc divided into angular degrees. A vernier upon which ten divisions correspond to nine divisions of the disc enables the observer to read tenths of an angular degree and estimate twentieths.

The tube is filled with water, and the zero of the instrument adjusted so that each half of the field of vision is equally illuminated. The tube is then filled with the liquid to be examined, placed in the instrument, and after having focussed the plate by means of the tele-

scope, the pointer is turned to the right or left according to whether the solution is dextro- or levo-rotatory, until both halves of the disc are again equally tinted.

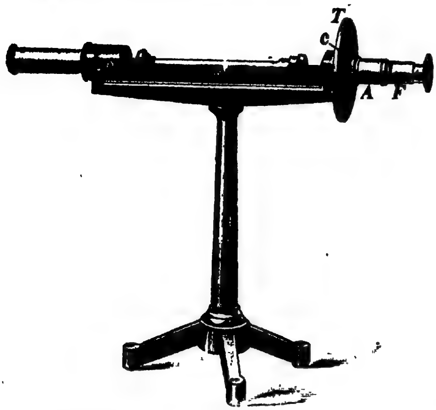


Fig. 13.—Mitscherlich's Polarimeter. P, polarizer; A, analyser; F, telescope; R, operating tube to hold turps to be tested.

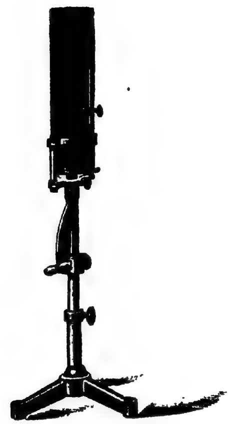


Fig. 14.—Sodium Lamp.

In the annexed figure the zero point of the vernier is not quite at 3° on the scale of the disc, and the eighth division of the vernier is the only one which coincides with a division of the scale—consequently the reading is 2·8°.

The instrument is constructed for homogeneous light. A sodium lamp must therefore be used as the source of illumination. The zero point, as in other half-shadow instruments, is found when both halves of the field are of the same tint.

TABLE XXIV.—ACTION OF POLARIZED LIGHT ON SPIRITS OF TURPENTINE.

	Temp. of Observation.	Limits of Concentration.	Signs.	Rotation $\alpha_{[D]}$.
Spirits of turpentine, American (*P. australis*)	20	d = 0·9104	+	14·147
Spirits of turpentine, American, *alcohol*	20	q = 27·78	+	14·173 − 0·0011782 q
Russian (*Pinus silvestris*)	24·5	d = 0·85	+	27·7
French (*P. maritima*)	20	d = 0·863	−	37·01
French, *alcohol*	20	q = 10·90	−	36·974 + 0·0048164 q + 0·00013310 q^2
„ *benzol*	20	q = 10·90	−	36·970 + 0·021531 q + 0·000067627 q^2
„ *ac. acetic*	20	q = 10·80	−	36·894 + 0·024553 q^2 0·00013689 q^2

Effect of Adulteration on the Optical Deviation.—The polarimeter has been recommended as an aid to detection of adulteration in spirits of turpentine, but its results require confirmation; by themselves they are unreliable, as there are both dextro- and levo-rotatory terpenes. In any case it has been shown to be impossible to distinguish even French (dextro) and American (levo) turpentines by this method.

Utz found that different samples of genuine spirits of turpentine from the same source gave such discordant optical deviations in the polarimeter that no information as to the purity of any given sample could be obtained by polarimetric methods alone.

According to the formula he gives for estimating the amount of the adulterant present, both it and the turpentine have a constant coefficient of rotation. Now this is not the case with turpentine at least. Aignan distinguishes three sorts of rosin oil, whose angles of rotation are given below:—

1. Choice white rectified oil	+ 72°
2. Fine white rectified oil	+ 32°
3. White rectified oil	+ 20°

It is only the first that is likely to be used for the purpose in question, and although its rotation is different somewhat from that of French oil of turpentine, it could easily be made equal to it by mixture with some of No. 2. A better test for the detection of rosin oil is as follows: The turpentine is distilled under a pressure of 60 mm., and the residue left at 100° C. is tested in the polarizing apparatus. The rotation with French turps should be to the left, but it will be to the right with over 5 per cent of adulteration.

Zune detects rosin oil by determining the refraction of the liquid. He distils 100 c.c. of the sample into four fractions each of 25 c.c.; the last fraction remaining in the flask contains the greater portion of the rosin oil.

TABLE XXV.—EFFECT OF THE ADULTERATION OF SPIRITS OF TURPENTINE ON THE INDEX OF REFRACTION.

	Index of Refraction.
French spirits of turpentine	1·47303-1·47420
American " "	1·47282
Rosin spirit	1·47491-1·48623
" oil	1·51468-1·58517
Spirits of turpentine + 2 per cent of rosin oil . . .	1·47191
Last fourth of distillate	1·47903

The refractometric method (Zeiss) is an extremely valuable method of examination, for the refractive indices of different turpentines differ over a very small range (1·470 to 1·473 at 50½° C.), and this, therefore, forms a good basis for the detection and estimation of adulteration. The *specific gravity* (*vide supra*) is almost an equally good deter-

mination, but is sometimes difficult to carry out on small amounts, though quantities as small as 1 c.c. can be employed by the use of special tubes. The Abbé refractometer gives also the dispersion which is sometimes of use. Both the specific gravity and refractive index of the saturated hydrocarbons are distinctly less than those of the terpenes, but the specific refractivity, depending upon both these factors, reduces the difference between the two classes of substances, as the process is one of division. To accentuate the difference Richardson devised a formula depending on the multiplication of these factors. The gravity of turpentine was about ·864, and of petroleum about ·801; the refractive index of turpentine is about 1·473, and of petroleum about 1·444. For the calculation of specific refractivities the Gladstone and Dale formula may be used, as there seems to be no very great advantage in using the more complicated Lorenz formula.

Utz found the index of refraction n_D (20° C.) of the fractions of (1) American and (2) Russian spirits of turpentine distilling at 150° C. to be 1·4164 and 1·4282 respectively. The fraction of the American oil boiling at 270° C. had an index of 1·4440, that of the Russian oil 1·4394, boiling-point 170° C., and 1·4422, boiling-point 180° C., whilst that of American and French spirits was found to be 1·4698 and 1·4714, a German sample giving 1·4748.

TABLE XXVI.—INDEX OF REFRACTION OF SPIRITS OF TURPENTINE AND ITS ADULTERANTS.

	At 15° C.	At 25° C.
Turpentine	1·4708-1·4735	—
American turpentine	1·4729	1·4668
Russian "	1·4747	1·4688
Rosin spirit, sp. gr. ·806	1·4488	1·4429
" " ·851	—	1·4649
" " ·867	1·4741	1·4678
" " ·902	Over 1·4895	Over 1·4895
Mineral oil " ·7897	1·4376	—
" Amer. " ·825	1·4613	1·4576
" " " ·835	1·4684	1·4646
" " " ·865	1·4840	1·4806
" " " ·885	Over 1·4895	Over 1·4895
" Scotch " ·840	1·4714	1 4675
" Russ'n " ·9058	1·4942	—
" " " ·9066	1·4943	—
Mineral oils	— 1·4776-1·4980	—
Rosin oils	— 1·5274-1·5415	—

Veze, Eustace, and Meline use the refractometer to determine the normal adulterants, rosin oil and rosin, and the abnormal adulterants, petroleum oil, shale oil, petroleum spirit, benzene, carbon disulphide. Each test includes (1) the distillation of 250 c.c. fractionated into five fractions of 50 c.c.; (2) the determination of the indices of refraction of fractions 1, 3, and 5 with Zeiss's butyro-refractometer

to four exact decimal places; the indices are included between 1·42 and 1·49; (3) the calculation of the percentage of adulterant according to the values found for the indices n^1 index of refraction No. 1, n^3 index of lot No. 3, and n^5 index of lot No 5.

$$\delta = n^3 - n^1 \text{ and } \Delta = n^5 - n^3.$$

By testing a prepared mixture they determined the ratio between the weight of the adulterant and the values of δ and Δ thus:—

$$\text{Rosin oil per cent H} = \frac{\Delta - 0{\cdot}0032}{0{\cdot}0037}$$

$$\text{Petroleum spirit per cent Esr.} \quad \frac{\delta - 0{\cdot}0007}{0{\cdot}0024}$$

For calculating the percentage of petroleum oil, shale oil, petroleum ether, benzine, carbon disulphide, similar formulæ have been worked out. According to these authorities we ought in any case to get

$$\Delta < 0{\cdot}0125 \text{ and } 6{\cdot}0000 < \delta < 0{\cdot}0010.$$

TABLE XXVII.—ABNORMAL OPTICAL ROTATION OF SIX SAMPLES OF AMERICAN SPIRITS OF TURPENTINE.

	1	2	3	4	5	6
Specific gravity at 15·5°	0·868	0·869	0·8685	0 870	0·8675	0 8675
Optical rotation	– 9°	– 7°	– 9°	– 6°	– 6°	– 8°
Refractive index at 20°	1·4721	1 4719	1·4720	1·4711	1·4725	1·4722
„ „ of first 10 per cent distilled	1·4709	1·4700	1 4699	1·4698	1·4700	1·4698
Boiling-point	156°	155°	156°	157°	155°	156°
Distilled below 160° per cent	43	45	44	45	44	44
„ „ 165° „	90	89	91	88	90	91
„ „ 170° „	94·5	94	94	93	95	93

No petroleum and no resin spirit was present, and so far as the various colour reactions can be at all relied on, there were no indications of so-called "wood turpentine". It is probable that the abnormal optical rotation is due to the presence of a large amount of spruce turpentine, to which no very great exception need be taken. In general properties there are no differences to be noted between these oils and normal ones ("The Oil and Colour Trades Journal").

Detection of Petroleum in Turps by Burton's Method.—Petroleum may be detected in turps by Burton's method: Run into a cooled flask attached to a vertical condenser 300 c.c. of fuming nitric acid of density 1·40. Drop slowly through a separating funnel into the flask (kept as cool as possible) 100 c.c. of the turps to be tested. Violent reaction ensues. The spirits of turpentine dissolves in the acid whilst the floating petroleum is removed by a separating funnel and measured.

With a petroleum addition boiling at 250° C., 34·1 per cent were got instead of 35 per cent, and when the boiling-point of the added

petroleum was 75° and 20 per cent of it were added, the analysis gave 17·9 per cent only, and 28 per cent when 30 per cent were present. A very similar process is described by Allen, who, however, uses 400 c.c. of fuming nitric acid instead of 300. An older method, proposed by Armstrong, depends upon the fact that oil of turpentine is polymerized by strong oil of vitriol, and converted for the most part into products which are not volatile in a current of steam. But as cymene is also formed in varying proportions similar to the paraffins, and like them, stable against sulphuric acid, the fuming nitric acid test is to be preferred to the vitriol test.

Action of Sulphuric Acid.—For the detection of petroleum products in turpentine Prof. Armstrong recommended treatment with sulphuric acid, which polymerizes the turpentine but does not affect paraffins. H. Herzfeld recommends the following process: 10 c.c. of the sample to be examined are slowly run into 40 c.c. of concentrated sulphuric acid. After ten to twelve hours 8 or 9 per cent of the turpentine separates, and the lower layer is dark brown in colour. The lower layer is run off, and 3 or 4 c.c. of fuming sulphuric acid is added to the residue. If the sample is pure not more than ·1 or ·2 c.c. of the turpentine will again separate. If mineral oils are present, the amount which separates will be much larger. Rosin oils and coal-tar naphtha cannot be detected by this test, as they are affected by the sulphuric acid.

Moreover, Scottish and other shale oils and spirits are far from consisting wholly and solely of paraffins. When, therefore, spirits of turpentine is adulterated with shale spirit, Burton's test must give quite fallacious results, as Scottish shale products abound in olefins on which nitric acid acts energetically. Nitric acid also acts energetically on certain of the constituents of Russian petroleum.

In a paper read before the Society of Public Analysts, J. H. Coste recently expressed the opinion that the process of polymerization and sulphonation proposed by Armstrong is in every way preferable to the various drastic methods suggested by later workers. A. K. Turner (in "The Oil and Colour Trades Journal," 15 August, 1908, pp. 503-6) states that the results by Armstrong's method obtained are invariably very low—at times as low as 20 per cent below the truth. Coste, in a further paper, read at a meeting of the Society of Public Analysts, draws attention to the fact that Turner there adduces the results of experiments with mixtures of kerosene and turpentine in which the amount of unpolymerized steam distillate is considerably less than the amount of kerosene actually present. He then states: "Apart from the fact that the experimental details differ materially from those described by Armstrong, the distinction made by that author between petroleum oil and petroleum spirit has been neglected. Armstrong, after stating that an exact distinction is difficult, adopts for the purposes of his paper the term 'petroleum spirit' for the portion of petroleum distilling in steam at the ordinary pressure, and 'petroleum oil' for the portion which is not so distil-

lable. Kerosene, an unusual adulterant, and one which is easily detected by practical distillation, is a mixture of substances only some of which can be distilled in steam." Details are then given, showing that kerosene only contains approximately 60 per cent of steam distillable oil, and that this only leaves about 5 per cent when treated as described by Armstrong. He proceeds: "The process adopted by Turner, of shaking with concentrated sulphuric acid, and measuring the separated top layer, which he calls petroleum, is more violent than Armstrong's. It may, as he states, yield results which approximate to the amount of petroleum added—in fact, it appears to do so; but these results are only due to a happy compensation of errors." Coste concludes his paper by stating that "he still maintains that Armstrong's method, based as it is on sound scientific principles, is capable of giving excellent results if properly used—that is, if the petroleum oil be determined by distillation of the original sample in a current of steam, and petroleum spirit by polymerization of either the distillate from this process, or another portion of the original". But Coste seems to base his arguments upon the unsound data that petroleum spirit consists wholly and solely of paraffins.

The Detection of Petroleum in Spirits of Turpentine.—Boehme recommends the following method for detecting and determining the presence of petroleum and benzol in oil of turpentine or turpentine substitutes: 20 c.c. of a mixture of 1 volume of fuming and 3 of concentrated sulphuric acid are placed in a 40 c.c. flask, the neck of which (10 c.c.) is graduated in fifths of a c.c., and 10 c.c. of the oil under examination are run in, the mixture being kept cooled, and the flask set aside for an hour when admixture is complete. At the end of this time the flask is filled up with concentrated sulphuric acid until all the separated matter is contained in the neck of the flask. After standing for two to three hours the insoluble portion (petroleum hydrocarbons) floating on the top is examined by the refraction test. The amount of insoluble matter furnished by pure oil of turpentine under the above conditions averages about 0·9 c.c. per 10 c.c., and the following results will indicate the presence of the amount of petroleum hydrocarbons specified: Separation of about 1·25 c.c. is equivalent to 5 per cent by volume of petroleum oils, 1·70 to 10, 2·00 to 15, 2·50 to 20, 2·80 to 25, 3·35 to 30, 3·75 to 35, 4·15 to 40, 4·50 to 45. If the amount is less than 1·80 c.c., the refractometer test is necessary, since some samples of oil of turpentine have been known to furnish 1·60 c.c. under the above treatment. In the refractometer test the insoluble matter from pure oil of turpentine should give a higher refractometer index than the original oil, whereas that from a sample adulterated with petroleum or benzine gives a lower reading. Rosin oil and camphor oil produce no change in this respect. The test is liable to fail when benzol and petroleum hydrocarbons are present in certain proportion, the one neutralizing the effect of the other. The determination of benzol in oil of turpentine by means of sulphuric acid is unreliable, different strengths

of the acid either attacking the benzol or polymerizing the oil of turpentine; and the Schreiber-Zetsche bromine method is little better when resin oil is present, though it will give good results for benzol and petroleum distillate otherwise. Boehme recommends a mixture of 10 c.c. of potassium bromide solution, and 10 c.c. of dilute sulphuric acid (1 acid, 2 water). A sample containing equal parts of oil of turpentine and benzol gave the bromine value [grammes of bromine per c.c. of liquid] 1·115, whilst that of the turps used was 2·25, so that the calculated proportion of benzol amounted to 49·56 per cent.

The Effect of Adulteration of Spirits of Turpentine on its Solubility in Glacial Acetic Acid.—The insolubility of petroleum in acetic acid may be used to detect petroleum in spirits of turpentine. Dunwoody uses 99 grammes of glacial acetic acid and 1 gramme of water. Absolute acetic acid ($C_2H_4O_2$) mixes perfectly in all proportions both with oil of turpentine and petroleum. But the above mixture, although it gives a clear solution with its own weight of spirits of turpentine, will not do so with petroleum. Table XXVIII shows how much 99 per cent acid is required to dissolve the undernoted mixtures of petroleum and turpentine:—

TABLE XXVIII.—AMOUNT OF 99 PER CENT ACETIC ACID TO DISSOLVE MIXTURES OF TURPS AND PETROLEUM IN VARIOUS PROPORTIONS.

	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Petroleum	1	2	3	4	5	7	8
Spirits of turpentine	9	8	7	6	5	3	2
Acetic acid, aqueous, required for solution	40	60	80	110	150	230	270

P. H. Conradson tests turpentine for petroleum by evaporating 50 c.c. of the sample down to 1 to 2 c.c. on the water-bath. If the sample be free from petroleum the residue dissolves in 9 to 10 per cent of glacial acetic acid, but if 10 per cent or more of petroleum be present the mixture remains turbid and separates into two layers.

Richardson has pointed out that the glacial acid dissolved petroleum as well as turpentine, and that no separation could be obtained without the use of a certain amount of water, and that with varying proportions of water the operator could obtain almost any figure he pleased, and when the conditions were so arranged that the correct results were obtained, this was not a satisfactory separation, as each of the phases contained both turpentine and petroleum. For acetic acid of 99 per cent strength, it was shown, however, that the temperature at which the mixture became clear had some significance, but it was only suggested as a qualitative test, and not recommended for quantitative work. A very similar state of affairs was found when methylated spirit was used, as in the case of acetic acid. Any result that was desired could be obtained by suitable dilution, and as the correct results were therefore only obtained by a compensation of errors, the figures were of no practical utility.

Determining Adulteration in Spirits of Turpentine by its Thermal Reactions with Bromine, etc.—Richardson tried to devise a method of obtaining a thermal value for these oils, but he found that bromine gave too violent a reaction, and when diluted with carbon tetrachloride gave results which were inconclusive. The use of antimony tri-chloride had, at first, appeared very promising, as with any one turpentine the amount of admixture of petroleum hydrocarbons could be accurately measured, these latter having no thermal value; but this method had unfortunately proved to be useless on account of large and curious differences in the thermal value of different samples of pure turpentine, even with the same iodine value, so that a very different table would be required for each turpentine.

Effect of Adulteration of the Iodine Value of Turps and of its Fractional Distillation Products.—The iodine value is the most reliable chemical test for adulteration in turpentines, the pure spirit having a value of 370 and the adulterants of 1 to 20, according to the proportion of olefines. The Hanâus' method was found to give very unsatisfactory results, and the Hübl and Wijs' methods give the best results. As this value is affected considerably by changes in temperature, a method of correction has been proposed in which olive oil is used as a standard, and by its variations a factor is obtained which can be used in the calculation of the iodine value of spirits of turpentines.

Effect of Adulteration on the Bromine Value of Spirits of Turpentine.—According to the "Pharmaceutische Zeitung" the best test is that with bromine. 100 grammes of pure oil will take up 254 of bromine. The best American and French oils will take up 230 grammes. To apply the test, dissolve 1 or 2 grammes of the oil in chloroform and add a solution of 5 grammes of potassium bromide and 10 c.c. of hydrochloric acid. Then titrate with a standard solution of potassium bromate until no free bromine is present. Some of the commercial turpentine substitutes take up no bromine, and all of them take up much less than the genuine oil.

Schreiber and Zetsche apply a similar test. Thus 1 c.c. of the sample is made up to 50 c.c. with 90 to 95 per cent alcohol; 20 c.c. of this solution are run into a gas cylinder with stopper of 75 c.c. capacity, 20 c.c. of a bromine salt solution and 20 c.c. of dilute sulphuric acid 1 : 3 added and shaken for half a minute. If the sample be pure complete declorization will take place. If it does not do so, the sample as a suspicious one is to be further examined. The test should be carried out in daylight and at a temperature of 20° C. The bromine salt solution is made by dissolving 15 grammes of potassium bromate and 50 grammes of potassium bromide in a litre of water, the bromine estimated volumetrically and the solution adjusted to 40·5 grammes per litre. Pure spirits of turpentine has a bromine value of over 2 grammes of bromine per c.c. oil, pure, but resinified spirits of turpentine may, however, have a bromine value of less than 2. On bromination of their fresh distillates they nevertheless give correct bromine values of over 2.

TABLE XXIX.—BROMINE VALUES (ADDITION AND SUBSTITUTION) OF COMMERCIAL TURPS AND TURPS SUBSTITUTE (VAUBEL).

	Substitution.	Addition.		Substitution.	Addition.
American 1 .	118·2	236·4	Russian 2 .	111·1	22·2
„ 2 .	115·9	231·8	Ordinary Polish	98·7	197·4
„ 3 .	117·5	235	Polish . .	111·1	222·2
French 1 . .	118·4	236·8	German . .	110·8	221·6
„ 2 . .	113·3	226·6	Pinoline F .	21·[illegible]	42·48
Grecian 1 .	120·6	241·2	„ S and L	45·24	90·48
„ 2 .	116·2	232·4	„ G .	18·84	37·68
Austrian . .	117·8	235·6	Rosin oil K .	32·61	65·22
Indian . .	116·7	233·4	„ Pale .	39·12	78·24
Crude DAB IV.	111·6	223·2	„ Dark .	56·85	113·70
Oxidized . .	111·06	222·12	Substitute ultra	5·61	11·22
Russian 1 . .	98·4	196·8	Terebentha .	4·8	9·6
„ 2 . .	98·7	197·4	Hallol . .	53·50	107·0

Effect of Adulteration of Spirits of Turpentine on its Flash-Point.—The presence of petroleum spirit lowers the flash-point, and renders its determination impossible at the ordinary temperature of 15° C. (59° F.). White spirit does not seem to affect the flash-point, whilst rosin oil raises it in direct proportion with its percentage content.

TABLE XXX.—EFFECT OF ADDITION OF WHITE SPIRIT, ETC., ON FLASH-POINT.[1]

Pure spirits No. 1	29·5° C.	Spirits No. 1 + 2 per cent Rosin oil	30·3° C.
„ No. 2	29·3° C.	„ + 5 „ „	31·2° C.
„ No. 3	29·5° C.	„ + 10 „ „	32·2° C.
Slightly old spirits	29·9° C.	„ + 15 „ „	33·2° C.
		Spirits No. 1 + 2 per cent white spirit,	29·0° C.
		„ + 5 „ „	29·5° C.
		„ + 10 „ „	29·0° C.
		„ + 15 „ „	29·2° C.

The nature of the adulterant may be detected by means of their oxidation products under the action of light. Two fractions of the sample to be tested are placed under similar conditions (temperature, evaporation, etc.), but one is exposed to light, the other is kept in darkness.

Effect of Adulteration of Spirits of Turpentine with Rosin Spirit on Colour Reaction of First Fractions with HCl *in Presence of Tin.*—Grimaldi determines the presence of rosin spirit in spirits of turpentine by fractionally distilling 100 c.c. of the sample over a blue gas flame, collecting the fractions at intervals of 5° C. up to 170° C. To the first five fractions an equal volume of hydrochloric acid is

[1] The low flash of the pure spirits is due to the French testing instrument giving lower results than the Abel tester.

added slowly and without agitation, and a small granule of pure tin, and kept in a water-bath for five minutes. They are then shaken and returned to the water-bath. The presence of resin spirit (pinolin) is indicated by a green colour which varies according to the percentage of rosin spirit present, whereas spirits of turpentine or mineral spirit gives a yellow to brownish-black coloration. This test reacts with 5 per cent of rosin spirit.

Halphen's Test.—Further, one drop of each fraction is tested by mixing it in a porcelain basin with 2 c.c. of Halphen's reagent (sulphur in CS_2) and a little melted phenol dissolved in carbon tetrachloride (1 in 4). A trace of bromine vapour is allowed to fall on the liquid, and in the presence of rosin spirit a lemon yellow passing to a malachite green colour will develop within half a minute. Operating on 500 c.c. of spirits of turpentine and testing the first 20 c.c. of the fractionation, resin spirit can be detected in a spirits of turpentine containing only 1 per cent.

Detection of Dissolved Rosin in Spirits of Turpentine.—By mixing turps containing dissolved rosin with an aqueous solution of potassium carbonate after standing for some hours, three layers are to be observed: (1) a colourless upper layer of pure spirit; (2) a deep yellow middle layer of rosin soap, water, carbonate, and turps; (3) a coloured lower layer of the excess of aqueous solution. By comparative testing of the sample against a pure sample containing 10 grammes of rosin per litre in graduated tube we get the volumes V and V^1 of rosin soap. The ratio of the vol. $\frac{V}{V^1}$ indicates the percentage of rosin in the sample. A 20 per cent solution of K_2CO_3 is used, and the separation is carried out in a water-bath kept at 70° C. for 30 to 48 hours (Veze and Eustache).

The Acidity of Spirits of Turpentine as a Guide to its Valuation.—It must not be forgotten that pure pinene, the chief constituent of spirits of turpentine, is neutral; commercial spirits of turpentine contains organic acids; resenic acids from the oleo-resin, pyrogenated acids, the formation of which is induced in the still; acids formed by the action of the air on the spirits of turpentine; acids which owe their presence to substances used for purposes of adulteration. Although often overlooked determination of the acidity or acid "value" of spirits of turpentine is a matter of great importance. It affords valuable indications as to the source, whether (1) old, or (2) recently but badly distilled, or (3) whether adulterated with crude rosin spirit or rosin oil. Table XXXI gives some determinations of the acid value of turps with $n/10$ soda, 4 grammes NaHO per litre. The test liquor is retitrated occasionally with standard sulphuric acid 4·9 grammes per litre, using phenolphthalein as indicator.

TABLE XXXI.—ACID VALUE, NaHO, OF SPIRITS OF TURPENTINE, ROSIN SPIRIT, ROSIN OIL (RABATE).

		Milligrammes NaHO per litre.[1]
I. Commercial Turps.		
Steam distillation of the purified oleo-resin	Gabriel, Col	248
	Labalaye	252
Naked-fire distillation of the crude oleo-resin	Sales	280
	Darmagnac	296
II. Old Turps.		
Labalaye, 1899, No. 1		600
" No. 2		896
Société Centrale des products Chimique, 1897		1645
III. Various Samples.		
Fresh turps from a single distillation (Sales),	first runnings	1106
" " "	middle "	154
" " "	last "	651
Fresh turps, single distillation	first runnings	625
" "	second "	150
" "	third "	3150
Rectified rosin spirit		7875
" oil		364

N.B.—The density of samples of spirits of turpentine so rich in acid is of no value in analysis. The figures show that steam distillation of the oleo-resin produces a superior essential oil. The first and last runnings should always be carefully fractionally distilled and rectified separately or mixed with the crude oleo-resin of a subsequent operation. Moreover, the middle runnings, whether obtained by steam distillation or by naked fire, may be put on the market directly as rectified spirit. The first portions of the first runnings of every charge is coloured green by copper salts from the side of the still and the coil. They may be decolorized by agitation with dilute nitric acid or with 15 to 20 per cent of sulphuric acid of 4·9 grammes to the litre.

Spirits of turpentine is adulterated with numerous substances, such as petroleum, coal-tar and shale naphthas, burning mineral oil, rosin spirit, fatty oils. A mixture of camphor oil and petroleum is said to be sold under the name of German spirits of turpentine.

Detection of Alcohol.—Alcohol is easily detected in spirits of turpentine. When shaken with water the pure spirit separates, leaving the water limpid, but if alcohol is present the latter gives a milky liquid which treated by potash and iodine yields iodoform.

Fatty Oils and Rosin Oil.—Spirits of turpentine containing fatty oils or 3 to 4 per cent of rosin oil leave a greasy stain on evaporation on filter paper. But old samples of spirits of turpentine behave similarly, whilst pure fresh samples leave no trace of any stain whatever. Fatty oils may also be detected by pouring a small

[1] To express these acid values in terms of potash, KHO, multiply by $\frac{56 \cdot 1}{40}$.

quantity of the sample into an excess of strong alcohol; the latter dissolves the pinene whilst the fatty oils are precipitated. The great acidity of even rectified rosin spirit will be seen from Table XXXI, and the acidity still further accentuates that of the turps sophisticated therewith. What is said to be current practice in France is the addition of high grade rosin oil. This sophistication is difficult of detection. However, if the proportion of adulterant be high, the sample leaves a spot on paper and a residue in the alcoholic extract. Here again Aignan uses the polarimeter and gives the following formula for the calculation of the percentage of high grade rosin oil :—

$$[\alpha_D] = 61^\circ{\cdot}30' \frac{8{\cdot}30}{5}h$$

$$[\alpha_D] = 61^\circ{\cdot}30' + \frac{6}{5}e$$

for ordinary rosin oil, and

$$[\alpha_D] = -61^\circ{\cdot}30' + \frac{3}{5}e$$

for rectified rosin oil.

The boiling-point should be above 150° C. and the acidity in grammes of potash per litre inferior to 1. Renard distils 250 c c. of sample, re-distils, and collects 10 c.c. This fraction mixed with 2 to 3 c.c. hydrochloric acid strong yields the following colorations :—

Pale Yellow.—Pure spirit or spirit with rosin oil.

Brown, passing to black after a few hours; spirits of turpentine adulterated with rosin spirit.

Fractional Distillation, etc., of Substitutes for Spirits of Turpentine and their Interpretation.—According to Coste the results of the distillation test do not afford a certain indication of the volatility at ordinary temperatures, the most important item from a practical point of view. A short-range boiling-point—as in the best samples of genuine turpentine—raises a reasonable presumption of a fairly uniform vapour tension during the whole process of evaporation. The specific gravities and refractive indices of these samples of substitutes are remarkably high for the range of boiling-points, assuming the liquids to consist essentially of normal or cyclo-paraffin hydrocarbons. The low iodine value—except in a sample which contained turpentine—precludes the presence of more than a small amount of either terpenes or olefines. Pure samples of several paraffin hydrocarbons likely to be present gave the following results :—

TABLE XXXIII.—PHYSICAL AND CHEMICAL PROPERTIES OF HYDROCARBIDES IN TURPENTINE SUBSTITUTES.

Formula.	Boiling-point.	Specific Gravity.	Refractive Index.
Octane. C_8H_{18} . .	125·5°	0·719	—
Nonane, C_9H_{20} . .	149·5°	0·722	—
Decane, $C_{10}H_{22}$ . .	173·0°	0·7456	1·4093
Undecane, $C_{11}H_{24}$.	194·5°	0·7581	1·4185

By acting on turpentine substitutes with a mixture of equal volumes of ordinary concentrated nitric and sulphuric acids, some samples are separated into three layers: (1) unaltered normal and cyclo-paraffins; (2) nitro-compounds of the homologues of benzene; (3) unaltered acid. Steam distillation will approximately separate the unaltered paraffins from the less volatile nitro-compounds. Coste therefore concludes that the high refractive indices and specific gravities are to be explained by the presence of homologues of benzene, such as meta-xylene, mesitylene, and cumene, and that the physical properties of a given sample and the determination of the iodine absorption value should afford considerable information as to its composition, so that if followed by a rational application of the following processes, its composition should be fully disclosed: (1) removal of terpenes and some olefines by polymerization with dilute H_2SO_4; (2) removal of remaining olefins with strong H_2SO_4; (3) nitration of aromatic hydrocarbons and separation by distillation of the unaltered aliphatic hydrocarbons from the products of nitration. Sulphonation with Nordhausen acid would probably be equally suitable.

TABLE XXXIV.—PHYSICAL AND CHEMICAL PROPERTIES OF TYPICAL TURPENTINE SUBSTITUTES (COSTE).

	1	2	3	4	5	6
Specific gravity	0·7923	0·8026	0·8006	0·8046	0·8051	0·8092
Refractive index	1·4424	1·4474	1·4455	1·4498	1·4498	1·4445
Flash-point (Abel)	81°	78°	84°	83°	85°	90°
Iodine value	5·4	6·1	5·5	7·2	6·3	19·4
Distillate from 100 c.c.	—	—	—	—	—	—
„ below 140°	3·0	4·5	2·5	2·0	2·0	1·0
„ 140° to 180°	71·0	57·5	65·0	96·0	96·0	50·5
„ total	74·0	62·0	67·5	98·0	98·0	51·5
Temperature of distillation for 10 c.c.	145·5°	145·8°	148°	144°	143°	156·5°
„ for 20 c.c.	150°	150°	152·2°	145·5°	145°	161·8°
„ „ 30 „	154°	156·5°	156·5°	146·2°	146°	167·3°
„ „ 40 „	157·4°	166·3°	161·3°	148·4°	—	174°
„ „ 50 „	161·3°	170·5°	—	149·9°	150°	179·7°
„ „ 60 „	168°	178·5°	175·5°	152·6°	152°	—
„ „ 70 „	174·5°	—	—	155·5°	154·8°	—
„ „ 80 „	—	—	—	159·5°	158·5°	—
„ „ 90 „	—	—	—	167°	164·3°	—
Percentage lost in two hours at ordinary temperature	40·5	39·5	34·5	40·4	40·9	36·9
„ in 4 hours	65·7	61·4	56·9	79·4	81·7	55·1
„ „ 6 „	81·9	74 2	71·1	99·7	99 8	65·4
„ „ 8 „	90·4	82·0	79·2	99·7	99·8	72·1
„ „ 24 „	98·5	91·0	91·3	99·7	99·0	89·3
Residue after polymerization	99·3	—	—	97·5	96·5	96·7
Refractive index of residue	1·4418	—	—	1·4508	—	1·4449
Upper layer, after nitration	80	78	84	58	51	—
Lower layer, „ „	27	26	22	46	47	—

TABLE XXXII.—OPTICAL DEVIATION AND COLOUR TESTS FOR DIFFERENT VARIETIES OF SPIRITS OF TURPENTINE AND ITS ADULTERANTS (VALENTA).

Spirits of Turpentine	n_D Temperature, 20·5° C.	Deviation in 100 mm. tube, 20·5° C.	Chloroform Solutio[n] 6 per cent Iodine. 1 part Iodine Solution. 2 " Oil. Shaken in cold.	Heated at 100° C. for 1 minute then shaken.	[..]rts Iodine Solution. [..]art Oil. [..]olled over a [..]unsen Burner [..]hen shaken.	Behaviour with 1 part of 1 per cent Gold Chloride Solution to 1 part Oil. Heated for 1 minute at 100° C. then shaken. Oil Layer.	Gold Solution.	Heated for a short time over a Bunsen Burner. Oil Layer.	Gold Solution.	
1 Lower Austrian fir	1·46603	− 38·5	dark brown-red	raspberry-red	[..]k raspberry-red	reduction	no decolorization	reduction	no decolorization	Colourless, pleasant smell, prepared in lab. from oleo-resin.
2 Lower Austrian	1·46781	− 34·9	"	pale raspberry-red	"	"	"	"	"	Colourless, best from Furtenbach, Vienna, Neustadt.
3 American	1·47004	+ 6·9	"	"	"	"	"	"	"	Colourless, best sort Furtenbach.
4 "	1·46761	− 36·5	"	"	"	"	"	"	"	Vienna market, prima, colourless.
5 "	1·47077	− 2·6	"	raspberry-red	"	"	"	"	"	Colourless, Vienna market, purchased as best.
6 French	1·46623	− 37·5	"	pale raspberry-red	"	"	"	"	"	Colourless, pleasant odour, prima, Vienna market.
7 "	1·47577	+ 17·1	"	yellowish	"	"	"	"	"	Yellow oil, twenty years old, greatly resinified.
8 Grecian	1·46652	+ 36·3	"	raspberry-red	"	"	"	"	"	Got from Furtenbach, colourless, peculiar smell, quite clear.
9 Larch	1·46751	− 13·1	"	"	"	"	"	"	"	Distilled in lab., colourless, boiling-point 150-167° (157° C.).
10 Pinene	1·46958	+ 17·5	"	"	"	"	"	"	"	From E. Merck in Darmstadt—prepared.
11 Russian	1·47331	+ 16·1	dark brown	pale yellow	[..]eddish-brown	"	decolorized	"	decolorized	Light yellow, peculiar penetrating odour, Furtenbach, prima oil.
12 Polish	1·47731	+ 16·5	"	yellowish-brown	"	"	"	"	"	Dark yellow, highly resinified, about twenty years old.
13 Hungarian	1·47321	+ 20·3	"	brownish-yellow	"	"	"	"	"	From Vienna market, Sax, and Kratzer, yellow with penetrating odour.
14 "	1·47468	+ 19·8	"	"	"	"	"	"	"	Dark yellow, twenty years old, highly resinified oil.
15 Rectified pine	1·47145	+ 18·9	"	yellowish	"	"	completely decolorized	"	completely decolorized	Almost colourless oil, penetrating odour, got from Hass in Florisdorf.
16 Russian	1·48894	+ 16·0	"	brownish-yellow	brownish-yellow	"	"	"	"	Twenty years old, orange-yellow, highly resinified oil, with penetrating unpleasant smell.
17 Camphor oil	1·49070	+ 10·7	brown	black-brown	black-brown	"	"	"	"	Green oil, aromatic odour, from Vienna market.
18 Pinolin, crude	1·48168	+ 1·0	"	dark green	dark olive-green	"	"	"	"	Dark brown, somewhat cloudy oil, with a slight smell of creosote from distillation of Lower Austrian oleo-resin.
19 " yellow	1·47999	+ 0·2	"	"	"	"	"	"	"	Yellow but somewhat cloudy oil, bought in Neustadt.
20 Refined rosin oil	1·53920	+ 38·8	"	black-brown	black-brown	"	not completely decolorized	"	"	Yellow fluorescent thick oil, clear, got from Goldbach.
21 Rosin oil, light	1·53781	+ 47·2	"	"	"	"	decolorized	"	"	Brown, not quite clear, viscous oil, got from Furtenbach.
22 " "	1·53999	+ 45·0	"	"	"	"	"	"	"	Another but darker sample from same source.
23 Rosin oil, refined	—	+ 58·0	"	"	"	"	"	"	"	Pale yellow oil, distilled in lab. over soda lye from blonde rosin oil, bl.-pt. 280°-450° C.
24 Rosin oil, green	1·48168	± 0·0	"	"	"	"	"	"	"	Green, clear oil, Furtenbach.
25 Petroleum	1·44899	± 0·0	brownish-violet	brownish-red-violet	brownish-red-violet	—	—	—	—	
26 Turpentine substitute	1·41203	± 0·0	reddish-violet	reddish-violet	red-violet	—	—	—	—	
27 Motor spirit	1·38941	± 0·0	"	"	"	—	—	—	—	

TABLE XXXV.—RECIPES FOR TURPENTINE SUBSTITUTES (ANDES).

Substance.	Turpentine Substitute No.							
	1	2	3	4	5	6	7	8
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Russian turps'	100	50	100	150	100	100	100	—
Solvent naphtha	100	100	—	—	—	100	—	150
Petroleum spirit . . .	100	100	100	200	200	—	100	50
Rectified rosin spirit . .	—	—	—	—	—	200	100	50
Benzine	—	—	—	—	—	—	100	—
Fennel oil	—	—	1·25	—	1	—	—	—
Anise oil	—	—	—	—	—	1·5	—	0·5
Citronella	1	—	—	1	—	—	1·25	—
Caraway oil	—	1	—	—	—	—	—	—

CHAPTER X.

CHEMISTRY AND DISTILLATION OF ROSIN.

Rosins are classified as (1) pale yellow, (2) yellow, (3) reddish-yellow, (4) brown or black rosin. If the injection water be not completely expelled the rosin is opaque. If the essential oils have not been completely eliminated the rosin is viscous and tacky. As it contains sand as it comes from the still such rosin has a peppery appearance. Hence the preparation of rosin includes (1) drying, (2) filtration, (3) moulding, (4) accessory bleaching. (1) *Drying* is done in the stills, by slightly increasing the fire heat as soon as the injection of water is stopped. With steam heating, drying is more difficult. Violette used superheated steam. Col runs the rosin out into a steam-jacketed truck of red copper. The steam jacket is connected with a steam pipe, and the temperature is kept high enough for the last traces of steam to be rapidly driven off. This is completely so when the fused material is perfectly tranquil. (2) *Filtration.*—To eliminate sand, shavings, pine needles, the fused rosin is passed through a wire-gauze sieve. The ordinary sieves are frames, the bottom of which consists of 150 to 250 wire gauze. These filters easily get choked and require scraping, which quickly wears them out.

Dromart designed a rotary filter to prevent choking. He runs the fluid rosin into a tank lined with sheet-iron, from which it flows through a valve into a horizontal wire-gauze cylinder which is slowly rotated. To run out the core left in the sieve the gouge is lifted, the cylinder and the plug are momentarily removed. Violette uses in his Hume factory an ingenious process of steam filtration. The rosin is run into a cylinder the bottom of which is furnished with a coarse linen cloth held by light lugs to hooks. The cylinder is first heated by a steam coil then charged with rosin. The air exit tap is shut and the steam inlet pipe opened. In a few minutes the rosin filters perfectly limpid, and as soon as the steam reaches the bottom of the cylinder the pressure is stopped. The cloth charged with sand and woody debris is detached and replaced, and the apparatus is ready for another operation. (3) *Moulding.*—The filtered rosin may either (*a*) be run directly into moulds; (*b*) into a tank whence it is lifted by dippers to charge the barrels; (*c*) into shallow cast-iron plates 20 inches × 4 inches; (*d*) into dismantling moulds in which the rosin is rapidly cooled in small quantities. The cakes obtained are sorted, placed by threes in the barrels, and amalgamated together by the rosin coming from the apparatus. (4) *Bleaching.*—Pale rosins are sometimes exposed to the solar rays in the sheet-iron trays just mentioned. They become still more pale, and extra pale rosins are so produced, selling at 18 to 20 francs, whilst ordinary rosins sell at 14 francs. But this process requires

perfectly dried rosin; it entails much labour and space and takes ten days. The pale rosins of the month of August may gain in value in the trays 0·5 francs per 100 kilogrammes, say 2½d. per cwt., and the April-May rosin 6 to 8 francs, say 2s. 4d. to 3s. 2d. per cwt. To make the yellow rosin used for torches, soldering metals, etc., the pale rosin is heated up with water and run into a large trough 13 feet long by 27 inches wide by 27 inches deep. Ten per cent of water is run on to the liquid rosin. Tumultuous boiling ensues and the mass swells. Two men stir it, breaking it up with spatulæ. The beaten-up mass assumes a honey-yellow coloration and becomes opaque. If too much water be used, liquid globules are left in the rosin which render it spongy. The opaque rosin still hot and fluid is run into moulds of wet sand, where it solidifies in masses of 10, 50, or 200 kilogrammes (22, 110, or 440 lb.).

Valuation of Rosin.—Rosins are valued in direct proportion to their limpidity, and in inverse proportion to their depth of colour. In sampling rosin, a block is detached, which is trimmed to a cube of 22 millimetres square. This operation requires a certain amount of practice; rosin being brittle it is more easily accomplished by using a knife with a heavy handle. If rosin be slightly pulverized it becomes white and opaque. Its transparency may be restored to it by moistening it slightly with alcohol and drying. The sample is then classified by comparing it in the light with standard cubes. The well-known American scale should alone be adopted. Certain dealers, however, do not scruple to adopt fantastical scales, so as to confuse buyers and profit by the confusion. But all rosin classifications have serious drawbacks: rosin is fragile, the edges and faces are irregularly dressed, the shades diminish in intensity under the action of light, which involves frequent classification. Moreover, the price of the standards is rather high, the series of fourteen cubes costing 16s. It might therefore be advantageous to replace the series of rosin cubes by a series of glass cubes tinted from pale yellow to black in accordance with the American typical standards.

The following are, in order of quality, good to poor, of colour pale to dark, the different brands of American rosin with the equivalent French classification of the same grades:—

TABLE XXXVI.—GRADES OF AMERICAN AND FRENCH ROSIN.

Marks.	American.	French.			
V A V	—	Window glass	F	Good No. 2	Brais demi noire et noire.
W	Water-white	Colophane	E	No. 2	
W G	Window glass	,,	D	Good strained	
N	Extra pale	,,	C	Strained	
M	Pale	,,	B	Common strained	
K	Low pale	,,	A	Common	
J	Good No. 1	Brai clair et arcansons			
H	No. 1	,,			
G	Low No. 1	,,			

Valuation of Spanish Rosins.—These are nearly all fine grades. They have fourteen grades, denoted by Roman numerals. Spanish grade V corresponds to about the American water-white, and they have no grades like the lowest. Several Spanish grades are of finer quality than the American water-white. There is little demand in Spain for fine rosins, so they ship them, as well as the spirits of turpentine, out of the country, to Germany, Portugal, France, and Switzerland. American common rosins are used. Both Spain and France have heavy duties on naval stores, which effectually protect the industries in those countries. Spanish producers have naturally been benefited by the higher prices of American naval stores, as have the producers of France. In France, though, there is more competition among the producers, who sell directly to the consumers, and cut beneath each other's prices in some degree. That country exported largely to England of late years as the result of the high prices prevailing.

Rosin Specification of the United States Navy Department.—The following are the rosin specifications of the United States Navy Department: (1) For all ordinary purposes rosin shall consist of equal proportions of grades "C," "D," and "E," known as "good strained rosin," "C" being the poorest quality, "E" the best of the three. (2) Rosin shall be graded by sample, a piece being cut from the top head of each barrel, seven-eighths of an inch cube, as nearly as can be done. Uniformity of size is important, as the thickness of the piece determines the shade of colour, and thus its value. (3) These cubes or samples are to be furnished by the seller free of charge, and will be referred to in deciding its grade. For special purposes, if required, the better grades are designated by the letters "F," "G," "H," "I," "K," "M," "N," "WG," and "WW," "WW" being the highest grade. (4) The rosin should be perfectly transparent. Its specific gravity should be between 1·04 and 1·15. Its melting-point should not be higher than 135° C.; it should dissolve easily in either alcohol or turpentine. A definite cause for rejection will be the presence of an appreciable amount of dirt or pitch. (5) Cubes of suitable sizes of the rosin offered under a bid shall be supplied by the contactor for chemical analysis, and if this analysis shows that adulterants of any nature have been incorporated in the rosin it will be cause for its rejection. (6) Requisitions should specify the grade, using the letter designation for description of quality.

Rosin Inspection and Valuation in the U.S.A.—The gauging of spirits of turpentine is not so picturesque as the grading of rosin. In the former work the Government method of gauging liquids is used, and that is all there is to it. With rosins it is different. From the time a barrel of rosin is placed upon the wharf until it goes aboard ship to be exported, it passes through many hands, but more depends upon the man who declares what it shall grade than anyone else. The inspector goes in among, say, 1500 or 1800

barrels of rosin, scattered over wide ground on a wharf. To inspect 1800 barrels a day is considered fair work, but some inspectors have passed 2600 in one day's time. That, however, is exceptional. With the inspector go two or three gangs of men and young boys. There is one gang to "uncooper" or unhead the barrels. When this is done a piece of rosin at least 6 inches square is cut from the contents of the barrel. This is handed to the young man who cuts out the samples. This is where the fine art of rosin sampling comes in. This sample cutter is an artist. He uses a sharp adze, and, taking the large piece of rosin of irregular shape in his left hand, he taps it gently with the sharp blade of the adze. This is done on four sides, and soon the rosin block begins to take shape. The chipping away of the rosin is kept up until a perfectly square block just a little short of an inch is produced. This is the rosin sample that is to be passed upon by the inspector. Hundreds of them can be cut with great rapidity, and when they are laid out together there will not be a difference of a sixteenth of an inch in their size. The sample is placed on the side of the barrel and the inspector comes by. Here is where his keen eye and his good judgment come into play. He carries with him a complete set of samples of the various grades of rosin.

There are thirteen of them. The palest rosins are the most valuable, and as they get darker in hue they become less valuable. The newly cut sample is held to the light beside the sample, and the inspector calls the grade. It is recorded by an assistant, and the inspector passes on to the next barrel, from which a large piece of rosin has been cut and the sample made from it. He grades this, and goes on to another barrel. This is kept up until every barrel has been opened and sampled. Behind the inspector comes a man who coopers up the barrels of graded rosin, and another man weighs them and marks the weight on the side of the barrels. A record of the inspections is kept, and this record goes to the factor. This inspector is paid 6 cents a barrel for inspecting the rosin by the factor by whom he is employed. The railroad upon whose wharf the rosin is placed pays a quarter of a cent a barrel for the inspection. This makes the total cost of the inspection 6¼ cents a barrel. The inspector has to pay all his helpers, and this amounts to a good deal. One inspector says his expenses amount to from 600 dols. to 700 dols. per month, while there are others who even pay out more than that. The inspector, after being elected to his office by council, has to make arrangements with the factors for employment. The work is divided about equally among the several inspectors. Some of them work for one firm alone, while others are employed by two or three factors. While the factor pays the inspector for the work that is done he charges the producer with the cost of inspection, and the man who ships the spirits or rosin has finally to pay for having it gauged or inspected at the port. The rosin samples are brought from New York to Savannah. These are the original types by which all the

inspections must be gauged. They cost 2 dols. 40 cents a set, and the sets have to be renewed about once each year. They formerly cost 5 dols. a set, but the price has been reduced. After reaching Savannah they are approved by the inspecting committee of the Savannah Board of Trade, and they can be used for grading the rosin sent here to be inspected and sold. After being elected by council, a naval stores' inspector has to give a bond of 2000 dols. that he will conscientiously perform his duties.

Refining Rosin.—Several processes have been indicated. In view of the numerous attempts which have been made to refine rosin so as to produce therefrom a good drying varnish, the following processes may be pointed out without expressing but a limited amount of belief in their efficacy :—

(1) It has been proposed to pass a current of chlorine through melted rosin ; the mass is acidified with sulphuric acid, washed with boiling water and finally with hot water containing nitric acid. (2) The rosin is heated with a solution of common salt ; it is then brought to the boil for a few minutes after adding a solution of chromic acid, or a solution of bichromate of potash and sulphuric acid, and the operation finished by washing with water rendered slightly ammoniacal. (3) Another process consists in heating rosin with a mixture of chalk, black oxide of manganese, and bichromate of potash and filtration through sand. (4) Or the rosin is heated with zinc dust with or without the addition of bisulphate of soda. (5) Attempts have also been made to use chloride of zinc and sulphuric acid at a high temperature. (6) The best process would appear to be to previously filter the melted rosin, then to heat it to 150° C. with 5 per cent of zinc chloride for one or two hours, and then to add about 12 per cent of bichromate of potash in powder. The whole is filtered after allowing the temperature to fall to 100° C. (7) Another process of purification consists in the use of sulphuric acid under pressure and at a high temperature. The process is conducted in an iron autoclave furnished with a steam jacket heated with superheated steam and capable of resisting a pressure of 12 lb. About 2 cwt. of rosin are run into the autoclave, and heat applied until the whole is melted, and when the pressure has reached 9 lb. the sulphuric acid is introduced. The whole is heated to 100° C. for an hour, then allowed to cool, and the product washed with boiling water. (8) Rosin was claimed to be obtained as colourless and transparent as glass by distilling the oleo-resin *in vacuo* with superheated steam (Hunt & Pochin's patent).

Not quite twenty years ago people began to increase the fusion-point of ordinary rosin which softens and becomes sticky even with the warmth of the hand, by melting it with compounds of lead, calcium, zinc, and strontium. The object is to make the rosin yield better varnishes. Then came Schaal, with his resinic acid esters, made from rosin, which, like the so-called hardened rosin, have the property of softening, but not dissolving, in spirit, so that varnishes

made from them become turbid on the addition of alcohol. The patent specifications describe the production of the esters, but with regard to the hardened rosins, although a few varnish-makers have written on the subject, much remains to be desired.

Of late these hardened rosins have gained an additional use for electrical purposes, and as the new processes are also useful to the varnish trade, it will be useful for us to consider them. Schaal, too, has improved his method.

Resinic acids from the coniferæ, fossil resins, or residues from the distillation of petroleum, brown coal, ordinary coal, turf or shale, are heated between 140° and 230° C. with an equivalent of metallic oxides and high boiling or non-volatile alcohols, until the combination of metallic rosinates and esters has taken place. To get the hardened rosins as neutral as possible an excess of alcohol is used. This excess is removed after the reaction is complete by high temperatures, with or without the addition of more metallic oxide. Distillation *in vacuo*, or the passing in of readily volatile substances, or indifferent gases or vapours, makes the product still harder. The metallic compounds used are glyceride and oxyhydrate of iron, manganese, chromium or lead, while the alcohols are glycerine, phenol, cresol; cane, grape, and fruit sugars. According to the proportions between the ingredients, various properties can be given to the product. Preponderance of metal gives the greatest hardness, but resistance to damp, soda, etc., requires larger quantities of the esters.

The Composition of Rosin has been the object of numerous researches. It is solid, transparent in thin slices, brittle, friable, and easily pulverized. As rosin melts it passes through different stages of viscosity, which fact renders the determination of its melting-point difficult. It is insoluble in water, completely soluble in benzene, methyl ethyl and amyl alcohols, ether, acetone and acetic acid. Petroleum ether (gasolene of 0·650 gravity) only imperfectly dissolves rosin, and even with a great excess there is always a residue: yet a solution of rosin in coal-tar or petroleum naphtha, if it at first gives a precipitate with gasolene, that precipitate dissolves on stirring in the excess of naphtha present. The acidity of rosin may be determined by dissolving 50 grammes of rosin in a litre of alcohol and titrating with $N/_2$ potash, 28 grammes of KHO per litre. The index of acidity or acid value, Table XXXVII, or the number of milligrammes of potash necessary to saturate a gramme of dry rosin, varies between 165 and 175, with an average of 170. Hot saponification with potash gives figures higher than the acid index. The index of saponification is about 180. In the hot state, therefore, the alkali not only saturates the free acid but also the combined acids in e.g. esters or ethereal salts. The ester value represents the difference between the acid value and saponification value. Henriques found a relation between the ester value and the residue insoluble in petroleum ether (gasolene). He also found lactonic acids in rosin. The lactones are compounds obtained by replacing in the more or less complex mole-

cule two hydroxyl groups, the one alcoholic and the other phenylic or aromatic acid, by an atom of oxygen. The simplest acid alcohol is lactic acid $CH_3 - CHOH - COOH$. Henriques concluded: (1) Rosin contains neither esters nor acid anhydrides. (2) Rosin consists of acids associated with unsaponifiable matter, neutral resins (or resenes). (3) The acids present in the crude resin may be classified into two groups according to their behaviour with petroleum ether, viz. soluble normal acids and insoluble abnormal acids. (4) The normal acids are the lactonic which yield insignificant ester values. On the other hand, the abnormal acids are the lactonic acids which give rather high ester values; the ester value should be replaced by lactonic values. (5) The proportion of insoluble abnormal acid is greater the darker the rosin. Very pale rosins which yield small residues with petroleum ether, gasolene, contain normal acids, dark rosins, abnormal acids. Tschirsch's researches may be summarized thus: (1) Rosin contains resinic acids and neutral resenes. (2) The crude oleo-resin does not contain lactonic acids, but heat may generate lactonic acids in rosin. (3) The resinic acids present in the crude resin are not organic acids, but bodies containing phenolic hydroxyl (OH), which gives for pimaric acid $C_{20}H_{30}O_2$

$$C_{20}H_{28}<^{OH}_{OH}$$

(4) Rosin contains neither aldehydes, acetones, nor methylic ethers. (5) Rosins contain non-saturated compounds, which implies the existence of double bonds in the constitutional formula. Rosin may be said to contain about 90 per cent of acid bodies and 10 per cent of resenes and unsaponifiable bodies.

Oxidized Rosin.—Levy examined the oxidation products of abietic acid from American rosin. Sodium abietate ($NaC_{20}H_{29}O_2$) was oxidized with dilute potassium permanganate solution, carbonic acid, separated unaltered abietic acid from the acidified solution, a resinous substance from which volatile acids (propionic and isobutyric acids) were separated by steam distillation. The product so formed was soluble in most resin solvents, but insoluble in petroleum spirit. It was also appreciably soluble in boiling water. A crystalline substance, melting-point 246° to 247° C., was obtained. This acid $C_{20}H_{34}O_6$ is a monobasic acid, of which the silver and barium salts were prepared in a crystalline form, which confirm those of Fahrion's results, who assumed the product of the permanganate oxidation to be tetra-hydroxysylvic acid, or tetra-hydroxyabietic acid, $C_{20}H_{30}(OH)_4O_2$. The portion of the oxidized rosin soluble in hot water seems to differ from this in its properties, and probably is an acid with ketonic characters, as it gave a reaction with phenylhydrazine acetate. The oxidation of tetra-hydroxyabietic acid can be carried still further by heating with permanganate solution or with nitric acid, resulting in the formation of crystalline products.

Solubility of Rosin in Petroleum Ether.—Schick found that a sample of rosin, which left behind 3·6 per cent. of residue insoluble in

petroleum spirit, dissolved completely (except 0·5 per cent) when heated therewith to 320° C.

Schick does not agree with Dieterich that the saponification—and ether—values of rosin should be disregarded. Moreover, his acid number obtained by the direct titration of rosin in alcoholic solution is lower than Dieterich's "acid number," and also the latter, again, comes out smaller than the saponification value determined in a manner analogous to that pursued in the case of fats, which is always uniform and very definite, whether the saponification be effected by the warm or cold method. He sees no reason for abandoning the ester value, simply because Tschirsch failed to detect esters in rosin. But little value is attributed to the iodine number, although it is an important circumstance that the iodine number of the dark resins that have been exposed to prolonged strong heat, comes out lower than that of the paler kinds; this is probably due to the absorption of oxygen by the rosin, as shown by Weger.

Finally, determinations were made of the refraction index of 20 per cent solutions of the various rosins in linseed oil, the results coming out as 90·7° to 92·3° at 40° C.—the refraction of the linseed oil employed being 71·5°. These figures point to the suitability of employing this test for approximate quantitative estimations of rosin in oils, as also for admixtures of resinate compounds in metallic linoleates. By this simple means figures are obtained which harmonize fairly well with those yielded by the Twitchell method. Heat, however, produces a modification of these constants when a high temperature is employed; thus, for instance, the 20 per cent solution of one sample in linseed oil, with an iodine value of 146·2, gave a deviation of 90·7°, whilst after heating the rosin for half an hour at 300° C., the iodine value fell to 101·7 and the solution gave a refractometer index higher by 2·5° than before.

Spruce Rosin.—P. Klason and J. Kohler prepared two isomers of rosinic acid from the rosin of *Pinus abies.* After distilling off the turpentine in a current of steam, the mass contains the alpha and beta rosinic acid, together with oxidation products and certain impurities. Treatment with alcohol and chloroform leaves the impurities behind. The solution is distilled to dryness, and the rosinic acids are dissolved out from the oxidation products by repeated digestions in petroleum ether, followed by fractional distillation. The rosinic acids distil over between 250° and 300° C. The distillate solidifies on cooling as a yellow mass. It is dissolved in alcohol, and on crystallization the alpha acid crystallizes first. It is dextro-rotatory and fuses at from 198° to 199° C. The beta acid, which crystallizes later, is purified by recrystallization from glacial acetic acid. It forms white needles, fusing at 167° C. The formula of the two acids is $C_{20}H_{30}O_2$.

Natural or Auto-Oxidation of Rosin.—Normal rosin contains 4 to 6 per cent insoluble in light petroleum, as much as 70 per cent on long exposure to air, the rosin becoming whitish and opaque and

losing its conchoidal fracture. Powdered rosin exposed to diffuse daylight gave 60 per cent of material insoluble in light petroleum spirit (whilst the same kept in the dark only gave 4½ per cent). This change is due to auto-oxidation analogous to the oxidation of turps when ozone is produced. The acid value is not affected, but the melting-point of the portion insoluble in petroleum is far higher than that of normal rosin. The composition of abietic acid is doubtful, $C_{20}H_{30}O_2$ (Fahrion) being generally accepted. Rosin exposed to air in a thin layer forms by auto-oxidation unstable peroxides of the composition $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$, insoluble in petroleum spirit, decomposing with liberation of water and formation of products soluble in petroleum spirit. The variations in the acid and iodine equivalents of commerce rosin are probably due to the presence of neutral bodies and their anhydro derivatives in various quantities. Two samples of abietic acid, melting-point 153°-154° C. and 179° C., gave figures agreeing with Mach's $C_{19}H_{28}O_2$. The acid value of both gave a molecular weight $= C_{20}H_{30}O_2$. The electrical conductivity of both acids after fractional neutralization with $\frac{n}{10}$ potash, Kohlrausch's method, gave molecular weight = 303; $C_{20}H_{30}O_2$ requires 302. Further experiments show that abietic acid is a carbocylic acid $C_{20}H_{30}O_2$. From the acid value of 170, rosin contains rather less than half its weight of dibasic abietic acid.

TABLE XXXVII.—CHEMICAL CONSTANTS OF DIFFERENT BRANDS OF COMMERCIAL ROSINS.

Rosin.		Acid Value.	Saponification Value.	Ester Value.	Iodine Value.	Authority.
Austrian		146·0	167·1	21·1	109·6-110·8	Schmidt and Erban
,,		159·3	175·5	76·2	—	Ulzer
,, Pale		163·2	—	—	—	Kremel
,, Dark		151·1	—	—	—	—
English		169·1	—	—	—	—
American		154-164·6	174·7-194·3	15·7-30	55-114	Lewkowitsch
,,		170·2	177·9	7·7	124·2	Fahrion
Rosin	"Wite"	160·8	177·6	—	184·7	Smetham and Dodds
	Nemo	162·0	176·4	—	181	,,
	W. W. Zante	154·5	174·3	—	158·5	,,
	N. Xeres	157·3	174·3	—	168·4	,,
	W. G. Wax	160·1	177·8	—	165·9	,,
Rosin acids from above	"Wite"	163·9	176·4	—	175·5	,,
	Nemo	163·0	175·3	—	166·8	,,
	W. W. Zante	159·1	167·5	—	154·9	,,
	N. Xeres	159·1	165·5	—	—	,,
	W. G. Wax	161·0	169·5	—	—	,,

	W. W. Zante.	N. Xeres.	W. G. Wax.
Iodine number (Hübl)—			
After 2 hours	115·5	114·3	115·5
,, 4 ,,	124·1	125·3	121·7
,, 18 ,,	158·5	168·4	165·9
,, 7 days	—	165·3	—

WIJS' METHOD—0·2 GRM. ROSIN TAKEN.

	5 mins.	10 mins.	30 mins.	1 hour.
Iodine absorption, W. W. Zante . . .	124·7	128·4	134·6	—
Iodine absorption, N. Xeres . . .	137·1	132·1	147·0	152·0

WIJS' METHOD—0·1 GRM. ROSIN TAKEN.

	10 mins.	20 mins.	30 mins.
Iodine absorption, N. Xeres	171·2	177·5	183·6
	1 hour.	18 hours.	48 hours.
Iodine absorption, N. Xeres	194·8	249·4 / 249·4	270·5

It will be observed that, as with the Hübl solution, the iodine numbers increased with the time occupied for the reaction, and with the excess of reagent.

Metallic Rosinates.—Rosinates, formed by the combination of rosin with certain metallic oxides, occupy a prominent position in modern varnish and paint manufacturing, and are now generally preferred as driers to other metallic salts, being, with the exception of the linoleates, more readily soluble in linseed oil, since the latter frequently require a higher temperature than the rosinates to effect solution, and this is apt to render the varnish darker. Then again ordinary metallic compounds are liable to form deposits in the varnishes made with them, this not being the case with rosinates. As no large outlay is necessary, paint and varnish manufacturers will doubtless find it an advantage to make their own rosinates, hence the two following examples:—

Manganese Rosinate.—12 lb. of soda ash are dissolved in water in a wooden tub, 4 feet high and 4 feet in diameter, which is then half-filled with water. The contents are boiled up with steam, and, when well boiling, 64 lb. of light, coarsely powdered rosin are slowly added. Care must be taken that no lumps form, as then it is very difficult to get the rosin to dissolve. If the mass froths up too much the steam must be shut off, but stirring must be redoubled. When all the rosin has been run in a further 5 lb. of soda are added and the whole boiled up until quite clear; steam is then shut off and the hot liquid allowed to rest half an hour for any impurities to settle. Meanwhile, in another slightly larger tub placed just below, 27 lb. of chloride of manganese are boiled in sufficient water to stand at 20-23·2 Tw. The clear solution is now run into the manganese solution with vigorous stirring, rosinate of manganese separating out in the form of a white flocculent precipitate. When all the rosin solution has been run in, the cask is filled up to the top with water; the precipitate is then allowed to settle, and after the supernatant liquor has been drawn off it is well washed three times, collected in a filter press, and dried at a temperature of 35° to 50° C. Manganese

rosinate forms a soft white or grey powder, quickly browning in the air, the yield on the above-mentioned quantities being 80 lb.

Lead Rosinate.—A similar rosin solution as for manganese rosinate is first made. 41 lb. of crystallized sugar of lead are dissolved in the precipitating cask; the process is then the same as above. In this case, however, the yield is 96 lb.

Rosin Distilling: British Method.—This industry has flourished both in England and Scotland for many years, Granton, near Edinburgh, and Glasgow being the chief centres of the industry. It has also been for many years an important industry in the East and South-east districts of London. The form of rosin still used is generally a vertical cylinder with rounded top and bottom with a height about twice its diameter. The bottom is sometimes flat, but that shape, for obvious reasons, is not to be commended. The capacity varies. Very large stills are in use in London (in factories such as those doing a large trade in axle grease or in those factories who supply axle grease makers who do not themselves distil). Such stills may take a charge of say 20 tons. Direct fire heat is applied to the bottom of the still. Occasionally a superheated steam coil is also used as an auxiliary to the fire heat. The rosin used is American. Mills gives the following products from 70 barrels: (1) spirit, 60 to 70 gallons, or 3·1 per cent; (2) rosin oil for grease making, 1600 gallons, or 85 per cent; (3) coke, 6 to 7 cwt. or 3·9 per cent; (4) weak acid, water, 40 to 50 gallons, or 2·5 per cent; gas and loss, 5·4 per cent. But in London the stills are not usually run so far as to produce coke, the object being to produce as a final residuum a medium hard pitch capable of being utilized as an electrical insulator. Mills thinks pure rosin would leave no residual carbon in the rosin still. The gas, of which there is but little, is highly inflammable, and dangerous fires have occurred through bringing a naked light too near the discharge pipe coming from the condenser. The gas is said to be highly anæsthetic, containing carbonic acid, carbonic oxide, ethylene, and pentane. The percentage of rosin oil and other marketable products got by distilling rosin vary with the method, the quality, and the source of the rosin.

Funck got the following results by applying fire heat to the bottom of the rosin still and passing superheated steam through an upper coil in the centre of the still, whilst passing steam through the entire mass of rosin:—

TABLE XXXVIII.—RESULTS OF THE DESTRUCTIVE DISTILLATION OF ROSIN.

	Per cen
Acid water below 165° C.	—
Rosin spirit —	15
„ oil below 290° C.	25
„ „ „ 315° C.	25
„ „ „ 350° C.	12
	77

The liquid pitch in the still is run off through a stop-cock.

German Practice.—Boleg recommends cylindrical, cast-iron, round-bottomed stills of 5 tons capacity, at least, when three-quarters full (74 inches × 94 inches), without lid, cast in one piece, but better, made in two pieces, the cylinder part strengthened below, made of boiler-plate, and the still stronger bottom piece. This form gives a large heating surface, quiet and even distillation, greater strength and durability. Being in two, casting is done more carefully, the bottom can be renewed or repaired, leakage is avoided if the flanged joint be packed properly with asbestos and red lead. The 12 inches high, cast-iron, domed head fixed by screws is fitted with a discharge manhole in rear, and at the side a safety valve in centre, and a flanged sleeve about 10 inches high and 14 inches wide, for fixing on the still-neck, which, best made of copper, should, to get a thin distillate, free from vesicular rosin, that is, particles of undecomposed rosin entrained in the path of the vapour of rosin oil, be at least 40 to 60 inches high, and fitted with baffles to cause the vapours to take a spiral course. The descending limb tapers to an internal diameter at the condenser of only 2½ to 3 inches. The condenser is an important item; a mere coil, however well cooled, is insufficient for products superior to wagon grease oil. A double condenser like that used in the turpentine still is required, because a superior distillate is got if the first run, acid water, rosin spirit, and intermediate oils, as well as the strong smelling spirit and light oil distillates and gases, formed during the whole distillation process, be led through a different condenser than that used for the main distillate, the light or blonde oil. A capacious condenser for the main distillate, a smaller one for by-products, and a third coil kept solely for the green oil at the end of the process are required. Simple fractional distillation generally suffices, but with large stills it is best to work with a partial vacuum, 6 to 10 inches of mercury, i.e. with continuous exhaustion of the vapours, so as to get a more perfect fractionation of the strong smelling spirit and light oils, by means of a double vacuum receiver, and exhaust, especially where paint oils are to be made, and in sundry rectification processes. The sufficient decomposition of the distillate is effected by adding 3 to 5 per cent of powdered quicklime and complete distillation to dryness. The large hearth is not too far from the open firebrick arch protecting the still bottom from direct impact of the flame. Lump coal, mixed with nuts, is the fuel used, the latter being increased as distillation progresses. The gases given off in the process are also burnt underneath the still and save about one-third of the coal bill—mixed but profitable method of firing. Side-flues, 6 inches wide and 16 to 18 inches high, one in a forward and one in a reversed direction, each side, should be provided for the sides of the still, and fitted with dampers for shutting off the fire at will. Except in France, American good strained rosin is that distilled. The barrels rolled or hauled up from the store to the still manhole are broken and the

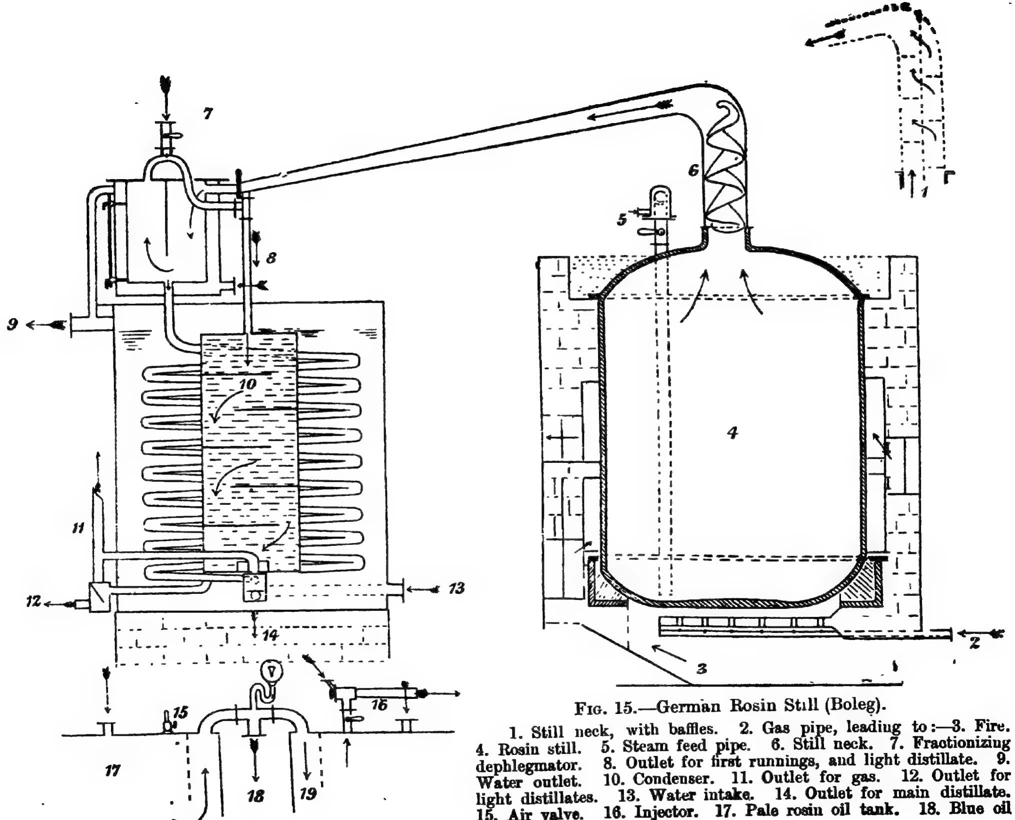


FIG. 15.—German Rosin Still (Boleg).

1. Still neck, with baffles. 2. Gas pipe, leading to:—3. Fire. 4. Rosin still. 5. Steam feed pipe. 6. Still neck. 7. Fractionizing dephlegmator. 8. Outlet for first runnings, and light distillate. 9. Water outlet. 10. Condenser. 11. Outlet for gas. 12. Outlet for light distillates. 13. Water intake. 14. Outlet for main distillate. 15. Air valve. 16. Injector. 17. Pale rosin oil tank. 18. Blue oil tank. 19. Light distillate tank.

rosin shovelled into the still, the staves and heads of the casks being subsequently steamed to recover the still adherent particles of rosin. [Those paint factories which make their own rosinate of manganese can, by treating their rosin cask staves with caustic soda lye, recover enough rosin, as rosinate of soda, to make, when precipitated by sulphate of manganese, all the rosinate of manganese which they require. Any excess of rosinate of soda can be made into soft soap for factory use, and the sound staves re-used for coopering purposes, the unsound ones being burnt underneath the boiler. The selling of rosin staves, with much adherent rosin, for firewood purposes, is at the present high market price of rosin a sure sign of bad management.] The fire is at first moderated to prevent priming. It is better to let interstitial water escape and rosin melt before putting on still-head, but as this may take several hours, $2\frac{3}{4}$ to 5 cwt. of paraffin oil are added per charge to obviate priming and the still-head can be at once fixed.

Working Details.—The still is filled in the afternoon and the rosin melted by 7 p.m., when the paraffin is added, the still-head fixed on, and the still left all night with a banked-up fire. At 4 or 5 a.m. the fire is made up, so that by half-past six, at the latest, the still begins to run, and distillation proceeds all day, the last runnings of blue oil being over by 8 p.m. If distillation be *in vacuo* it will be over two hours earlier. The liquid residue is then transferred by an injector into the separate still, solely used for distilling green oil, and the main still recharged next morning with ready melted fresh rosin. Where turpentine is distilled, the rosin left in the turpentine still can be run into the rosin still, after well ventilating the latter for about a quarter of an hour to prevent risk of explosion, and worked all day, the operation concluding at 9 or 10 p.m. This arrangement dispenses with all night work, stillmen, for the sake of extra overtime, being apt on day shift to unduly prolong operations. Moreover, unless there are night factory superintendents the stillman is not under such supervision as he is during the day, and is apt on occasion to force his stills in the early morning to make up for wilful neglect or irregular firing in the earlier hours of the night when he left the stills to take care of themselves. But by the arrangement just described this is obviated. Working thus, the stills can be charged four times a week, improving the quality of product and economizing in labour, repairs, etc., besides increasing the output. The residue from eight stills is united, and distilled, in smaller cast-iron stills, over direct fire and either to complete dryness or else to within a few per cent of green oil, the residue in the latter case being a more or less solid pitch suitable for working into black ships' varnish, shoemakers' pitch, and similar purposes. To prevent incrustation the stills should be cleaned out after every second distillation. This addition of paraffin oil yields better and paler products, free from vesicular rosin, carried over in the train of the vapour of the rosin spirit, and rosin oil, and thus more suitable for all usual purposes,

besides increasing the yield of pale oil by about 5 per cent. The yield from 5 tons of rosin so distilled averages: (*a*) 6 to 8 per cent of rosin spirit and acid water; (*b*) 50 to 55 per cent pale rosin oil, for refining; (*c*) 20 to 25 per cent of blue oil for the same purpose or for wagon grease; (*d*) 6 to 7 per cent of green oil for working up into wagon grease and carbolineum—i.e. a total of 80 to 82 per cent of distillate, leaving 15 to 18 per cent of residue, of which 5 to 7 per cent is utilizable gas and the remainder almost worthless. (The lime spoils the pitch.) To economize time and improve the quality of the products the final fractions (green oil) are distilled in separate stills.

The gas, of which there is but little, is highly inflammable, and dangerous fires have occurred through bringing a naked light too near the discharge pipe leading from the condenser. It is said to be highly anæsthetic, containing carbonic acid, carbonic oxide, ethylene and pentane. The percentage of rosin oil and other marketable products vary with the method, the quality, and the source of the rosin. Thus 1000 lb. yield:—

TABLE XXXIX.—RESULTS OF DRY DISTILLATION OF ROSIN PER 1000 LB.

	Herzog. lb.	Winckler. lb.
Crude rosin spirit and acid water	90-100	90-100
„ „ oil	720	712-760
Pitch	80	80

TABLE XL.—RESULTS OF DRY DISTILLATION OF ROSIN PER 100 LB. OF ROSIN DISTILLED.

	Per cent.
1. Acid water (green acetic acid)	2·0
2. Crude rosin spirit (D = 0·940)	5·0
3. Light oil (0·960)	10·0
4. Crude „ (0·980-0·990)	60·0
5. Brand „ (0·990-1·000)	5
6. Coke	2·5
7. Loss and impurities	17·5

The 60 per cent crude oil left on rectification:—

TABLE XLI.—RESULTS OF RECTIFYING THE (60 PER CENT) CRUDE ROSIN OIL OBTAINED IN TABLE XL.

	Per cent.
Light rosin spirit, specific gravity 0·880	4·0
„ oil, specific gravity 0·880-0·950	20·0
Middle „ „ „ 0·950-0·980	60·0
Brand „ „ „ 0·980-1·000	13·0
Coke	0·5
	97·5

Note especially that the rectification of the crude oil yields 4 per cent rosin spirit. It is a common saying amongst rosin still-men, that however often they redistil rosin oil they always get a certain amount of rosin spirit. Whether this is produced by "cracking" of the rosin oil or is merely due to imperfect fractional distillation in the various operations is a point which requires investigation.

The middle oil freed from its acid ingredients, 12 per cent, gave refined rosin oil.

Kramer and Flammer distilled 5 metric tons of rosin *in vacuo* with the following results:—

TABLE XLII.—RESULTS OBTAINED BY THE FRACTIONAL DISTILLATION OF 11,000 LB. ROSIN *IN VACUO* (KRAMER AND FLAMMER).

	Lb.	Per cent.
Rosin spirit	330	3
Rosin oil, blonde (yellow coloured)	5500	50
„ blue	1870	17
„ green	1650	15
	Total	85

Schweizer got the following percentage results:—

TABLE XLIII.—RESULTS OBTAINED IN THE DESTRUCTIVE DISTILLATION OF ROSIN (SCHWEIZER).

	Per cent.
Crude light rosin oil (rosin spirit, D = 0·891-0·896)	11·25-12·0
„ heavy blue rosin oil (0·815-0·935)	49-50·5
Brown rosin oil ("train" oil) (0·935-0·940)	10·25-10·65
Pitch	18-19
Acid water	5·5-5·8

Dr. Thenius' figures for 1000 lb. of rosin are:—

TABLE XLIV.—RESULTS OBTAINED IN THE DESTRUCTIVE DISTILLATION OF ROSIN (THENIUS).

	Lb.
Pyroligneous acid	57
Crude rosin spirit of ·89 specific gravity	114
„ blue rosin oil of ·93 specific gravity	500
„ rosin oil ("train" oil) of ·94 specific gravity	104
Pitch	185
Gas	40

Boleg's figures for the same, distilled, however, with from $2\frac{1}{2}$ per cent to 5 per cent of paraffin oil, to prevent frothing, are as follow:—

TABLE XLV.—RESULTS OBTAINED IN FRACTIONAL DISTILLATION OF ROSIN (BOLEG).

	Lb.
Crude rosin spirit and water	60-80
Yellow crude rosin oil	500-550
Blue „ „	150-200
Green „ „	60-70
Residue (valueless)	150

The figures depend upon many causes, such as the form of still and the temperature.

The distillation of rosin by superheated steam is not often practised except as an aid to fire heat, and its interest is as yet chiefly theoretical. A plant for the distillation of rosin *in vacuo* by aid of superheated steam (Fig. 16) has been constructed by Kramer and Flammer;

the results are tabulated above, but Schweizer says there is no advantage neither *in vacuo* nor by injection of CO_2, as the still is almost from the outset full of its own vapours to exclusion of air. Neither has distillation under pressure (p. 137) yet been adopted, and the most important method of preparing rosin oil is undoubtedly fractional distillation over a naked fire, either of coal or of fuel provided by the gases escaping from the distilling rosin itself. The lower part of the still is usually prevented from coming into contact with the flames by a perforated baffle plate. The still is of iron, either wrought or cast, the former being preferable. They are used in all manner of sizes, from a capacity of 2 cwt. to one of 20 tons. The bigger they are the better, provided they can be filled. A large still is far more easily managed than a small one, and the course of the distillation is

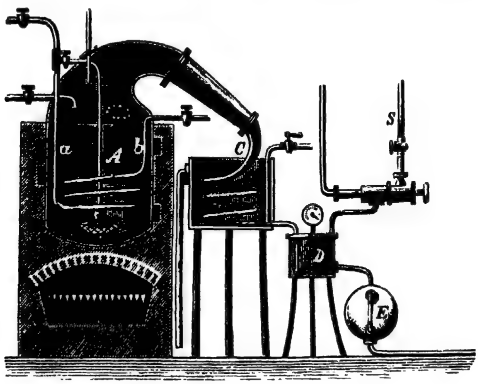


FIG. 16.—Kramer and Flammer's Vacuum Rosin Still. *A*, still; *a*, *b*, superheated steam coil; *C*, condenser; *D*, *E*, closed receivers. A steam ejector *S* works in *D*. The reaction gas is brought from *E* and burned underneath the furnace.

much more regular and certain. The best rule is to have a still capable of holding 5 cwt. for every 4 cwt. of charge. This obviates the risk of boiling over, as it allows room for frothing. But this should be guarded against. It is sometimes difficult to prevent priming, but it is far more difficult to stop it once it has started in full swing. The abrupt slope of still neck (Fig. 16) courts priming.

The condensing arrangements are of great importance. For the best work a simple worm-condenser is only sufficient if of great length. Two condensers should be provided, one for the rosin oils and the other for the earlier distillates. It is easy to arrange valves so as to turn the current of vapour from one condenser to the other at the right moment. A large tap must be provided in the bottom of the still for running out the pitch at the end of the distillation. In some works it is baled out through a manhole, with great waste of time and labour. Sometimes it is allowed to cool in the still and

then picked out, but the sharpening of the picks is an expensive item unless there be a smithy on the works. The pitch is full of sharp sand which soon wears them away. Moreover, men at work in the bottom of a large still cannot very well be supervised.

The Rosin Oil Industry in France: Present Practice.—In 1828 Etienne, a druggist, at Monte de Marsan, Landes, took out a patent for converting rosin into an oil, which he termed pyrogenated. By distilling rosin over lime and fractionating the products, he produced limpid and transparent oils. The same processes are still in use in the Landes factories. These factories, to the number of six, are Farbes, Albert, Lesconzeres de Lostatot at Monte de Marsan; Ponte at Dax; Mespliede at Lesperon; Castaigrede at Pissos. The French annual production may be estimated at 10,000 metric tons at the former average price of 10s. a cwt. The theory of the action of lime in the rosin still has not yet been satisfactorily determined. But it is right to say that under the action of heat the lime combines with the rosin acids, the base having a tendency to combine with the least volatile acids. The most fluid and volatile hydrocarbides distil over quite; in the beginning the differentiation of the distillates is facilitated. By forcing the heat towards the end of the operation, the lime and rosin soaps then undergo destructive distillation and produce green and blue oils. Lime increases the fluidity of the resulting oils, but the more lime added the more rosin soap is produced and the larger is the amount of dark oils towards the end of the distillation. Beyond a certain amount of lime the greater fluidity of the oil is not compensated by the drawback of such a large quantity of dark-coloured last runnings. If the amount of lime to be added were estimated on the quantity necessary to form a neutral calcium rosinate, far too much would be used. With pimaric acid the reaction may be expressed thus:—

$$\begin{array}{ccc} CaO + 2(C_{20}H_{30}O_2) & = & H_2O \;+\; (C_{20}H_{29}O_2)^2Ca \\ \text{Lime} + \text{Rosin} & & \text{Water} + \text{Lime Rosinate} \\ 56 + 604 = 660 & & 18 \;+\; 642 = 660 \end{array}$$

Say 56 of lime for 604 of rosin, or 9·3 per cent. The quantities of lime which suit best vary between 1 and 2 per cent on the weight of rosin. The rosin oils from both lime distilled and non-lime distilled rosins may be rectified, but the products from lime distilled rosins are much more fluid. Towards the end of the distillation the bulk in the still diminishes and the temperature reaches 500° C. (932° F.). The organic compounds with a lime base are then reduced chiefly to carbonate of lime, which retains a portion of the oxygen contained in the rosin.

The small French rosin still consists of a lower hemisphere (the body of the still) which is filled with rosin and covered with a copper hemisphere, the still-head communicating with a copper coil immersed in a trough full of running water, the body of the still when full of raw material containing about 27 cwt. of rosin. The fire of spent

pine-wood is lighted under it without fixing on the still-head to prevent priming and let the water evaporate. When the rosin is melted the still-head is fixed to the body of the still and the joint is simply luted with a paste made of lime and clay. All danger of explosion is thus avoided, because if the tension of gas be too great the still-head is simply blown off and the gas escapes into the air. Directly the still-head is fixed on and luted distillation ensues and is carried on (*a*) rapidly, or (*b*) very slowly, according to the quality of the oils which it is desired to get. If it only lasts three or four hours the oils are "hard" or "heavy," i.e. thick, viscous, and of density 0·980 to 0·990. Slow distillation lasts twelve to thirteen hours or longer; in that case the oils pass over much paler and in a more limpid and less viscous condition. They are the soft or light oils. Their fluidity may be increased by mixing with the rosin 1 or 2 per cent of finely divided quicklime previous to charging the still. Fractions of different colours, densities, and chemical composition are thus obtained according to the stage of distillation at which the still has been "cut" in producing the fraction. The distillate is run into a receiver with a tap from which it runs into casks.

Quick Distillation.—1325 kilogrammes are rapidly distilled in from three to three and a half hours. There is then got consecutively (1) 30 kilogrammes of a light rosin spirit boiling between 108° and 150° C., a mixture of (toluene and retinyle), which when rectified gives rectified rosin spirit used in industry to replace spirits of turpentine and by railway companies to clean parts of engines; (2) 975 kilogrammes of a pale oil, "hard," heavy, viscous, and thick; (3) 100 kilogrammes of blue oil of same quality, both sorts being used for grease-making. At the bottom of the still is a residue (4) of coke, solid, compact, and hard which is only got out with pickaxe or cold chisel, which with the incondensable gas makes a waste of 221 kilogrammes, or 16 to 17 per cent according to purity of rosin employed. Instead of blonde oils paler "soft" ones may be got by distilling more slowly and keeping the condenser well cooled.

TABLES XLVI AND XLVII.—RESULTS OF (*a*) QUICK AND (*b*) SLOW DISTILLATION OF ROSIN.

(*a*) Quick Distillation—1350 parts Rosin yielded :—	(*b*) Slow Distillation—1325 parts Rosin and 13 parts Lime yielded :—
30 parts rosin spirit.	30 parts rosin spirit.
975 " " oil, blonde.	250 " " oil, blonde.
100 " " " blue.	400 " " " white.
221 " pitch and loss.	160 " " " blonde.
	140 " " " blue.
	80 " " " green.
	278 " pitch and loss.

In the rapid distillation of rosin (in four or five hours without adding lime) the distillate consists of a thick, viscous liquid (*hard rosin oil*). The users of this oil are not numerous; it is used, in

admixture with other rosin oils, in the manufacture of rosin grease—the so-called antifriction greases. One of these is said to be made as follows· Pulverized and sifted slaked lime, 1 cwt.; pale rosin oil, 2 cwt.; hard rosin oil, 4 to 5 cwt., coloured with a little blue or green rosin oil. Such a formula is, however ridiculous; a rosin grease, as will be seen later on, need contain no more than 2 or 3 per cent of lime. Slow distillation has the following advantages over quick distillation: (1) The course of the distillation is more easily regulated and the products are more easily separated. (2) Overheating is less frequent. (3) There is less mechanical carrying over of unchanged rosin, consequently the oils have less acidity and are less viscous. The empyreumatic odour of the products is less accentuated. (4) Finally, rapid distillation increases the proportion of the initial and final products, water and light spirit on the one hand and dark oils on the other, at the expense of the middle runnings of pale oil. The shape of the still and the way in which heat is applied are important. By carefully regulating the temperature, and by rapid or slow condensation of the vapours, the relative proportions of light and heavy products of rosin distillation may be very appreciably modified. Great heat long applied to a deep still in which the vapours fall back several times before passing to the condenser diminishes the proportion of colophene, but notably increases the extreme products of the series between terebene and metanaphthalene. Rosin is distilled in France in cast-iron stills of 20 hectolitres, 440 gallons capacity, and thus capable of taking a charge of 2 tons of rosin. The body of the still is, generally, hemispherical. However, a Landes factory has experimented with an elongated, deep still, so as to lessen the space occupied. [Such a type of still will, of course, tend to "crack" the rosin oil and give a large yield of rosin spirit.] The object to attain is evidently a practical shape with the maximum of heating surface. Take a still consisting of a hemisphere and a cylinder of the same radius x, the height of the cylinder being y, the heating surface is then

$$S = 2\pi x^2 + 2\pi xy = 2\pi x (x + y).$$

The total height of the still is thus limited (1) by the furnace, and (2) by the upper level of the mass of masonry; hence,

$$x + y = H \text{ and } S = 2\pi Hx.$$

The heating surface varies, therefore, with x and becomes a maximum at the same time as x. Th s latter quantity attains its greater value for $y = O$, hence $x = H$. In the present instance the hemispherical form gives the maximum of heating surface. *Generally stills are grouped in pairs for the one still-head and condenser.* One of the stills is cleansed, then filled with rosin, while the other is being charged. Wrought-iron still-heads become corroded in a few days and numerous mishaps occur. Moreover, the pyrogenated acids yield iron salts, which contaminate the oils, rendering them dull and rusty. The still-head of red copper is alone used nowadays. If

there be back draughts, vapours slacken and much incondensable gas issues. The back draughts at this temperature are not very appreciable, because the last runnings are of high boiling-point and thus easily condensable. This is not so, however, if boiling occurs in the first part of the distillation. A thermometer ought always to be placed in the condenser vat. A continuous method of rosin distillation, invented thirty years ago by Carde, has not been generally adopted. The rosin is melted in A and flows from time to time by the valve *b*. The tap *c* is kept open and the heavy liquids pass over into C. In such conditions water, light spirit, and pale oil run continuously from the still B, whilst dark oil flows from the still C.

Details of French Distillation Process with Lime.—The still-head is fixed on the body of the still, filled with 2 metric tons of rosin, to which 20 kilogrammes, say 2 per cent, of quicklime has been added. The still-head is luted to the body of the still with potter's clay. The still mounted on a fire bridge is heated by wood. However, Farbes of Monte de Marsan utilizes the gas from the destructive

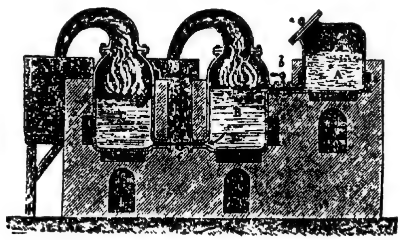


FIG. 17.—Carde's Rosin Still.

distillation of pine-wood. The fire is lighted at 3 o'clock in the morning and the heat regulated moderately until the rosin begins to melt—in about three hours.

The fire is urged until fusion is complete, then moderated as soon as distillation commences. There distil in succession (1) incondensable gases; (2) acid water containing acetic acid but in too small quantity generally to be profitably converted into acetate; (3) rosin spirit, a brownish-red mobile liquid with a strong, empyreumatic odour; (4) brown oils; (5) pale oils; (6) blue oils; (7) green oils. Water, gas, volatile acids, bulk largely at the beginning of the distillation, but these substances continue to distil during the whole operation and contaminate the oils. The latter are collected in a cast-iron tank, with a lower orifice for the exit of the water and an upper orifice for the evacuation of the oil. The distillate runs from 6 a.m. to 6 p.m.

The products of the dry distillation of rosin are, as will be seen, many and varied. Some are solid, rosin, lime, a mixture of coke and carbonate of lime, detached by picking from the side of the still in too quick distillation by overheating. Yet it is desirable to facilitate the

exit of the vapours from the still by a suitable form of still-head, which is chosen wide, flat, and the lower face with an accentuated slope. Copper coils are also preferred to iron coils. However, the last metal is sometimes utilized for the coils of rectifying stills, the oils to be then condensed being but feebly acid. Often towards the close of the destructive distillation the water of the condensing vats is in full boil; the condensed distillate contains water, acetic acid, volatile acids, aldehydes, hydrocarbides. The latter are especially numerous, and the chief may be resolved into two groups: (1) heptane C_7H_{12}, octane C_8H_{14}, and spirits of turpentine $C_{10}H_{16}$, which form the bulk of rosin spirit; (2) diterebenthyl $C_{20}H_{30}$, diterebenthylene $C_{20}H_{28}$, didecene $C_{20}H_{36}$, colophene $C_{20}H_{32}$, the chief constituents of rosin oil. Finally, the gaseous products escaping condensation are carbonic acid CO_2, carbonic oxide CO, methane CH_4, ethylene C_2H_4, butylene C_4H_8. The average price of first quality crude oil until the recent great rise was from 18 to 19 francs the 100 kilogrammes at the rosin distillery, and the profit and loss account was as follows:—

TABLE XLVIII.—PROFIT AND LOSS ACCOUNT OF A FRENCH ROSIN DISTILLERY.

	Francs.	Francs
Receipts.		
5 kilogrammes rosin spirit at 0·25 fr.	1·25	
80 ,, ,, oil at 0·19 fr.	15·2	
	——	16·45
Expenditure.	Francs.	
100 kilogrammes pale rosin	10·00	
Packing 1 barrel, 3 fr. for 300 kilos	1·00	
Carriage of rosin	0·5	
Fuel	1·0	
Labour	0·5	
Package for 80 kilos of oil	2·5	
	——	15·50
Profit per 100 kilogrammes of rosin distilled		0·95

The products obtained in distillation and their percentage:—

	Lb.
Acid water	5
Rosin spirit	3·5
Pale rosin oil	60
Green and blue rosin oil	20
Coke and volatile gases	10
	100

The white oils are the most abundant, amounting to 22 to 24 cwt. out of 32. They have a brownish-yellow tint, and are very fluid. Their density varies from 0·990 to 1·000. *They will not congeal even in the greatest frost.* They have good lubricating qualities, but, unfortunately, they *resinify* very quickly in contact with the air; and for this reason, and their strong odour, the use of them for lubricating purposes has always been limited. The railway companies and mine owners, however, use them very largely after having mixed them with from 25 to 50 per cent of colza or mineral oil. They

are also used either alone or mixed with linseed oil in making printing inks. (This treatise, Vol. I, Chap. IV, pp. 62-71.)

The blue oils are the distillation products which pass over immediately after the white oil. They have a very decided bluish fluorescence, and a density much the same as the white oils. Finally, when the distillation is nearing its end the green oils come over, which have a still more decided shade and a beautiful green fluorescence. They are always mixed with a large proportion of water, from which it is often difficult to free them. These oils are more fluid than the white oils; in fact, they contain a strong proportion of spirit due to the commencement of the pyrogenation of the colophene by reason of the high temperature to which it is then submitted in the distilling apparatus. The blue and green oils are used for general lubricating purposes.

It is difficult to assign a fixed chemical formula for each of these categories of oil. The composition of each varies with the proportion of carbon and hydrogen at every operation, since it depends upon the manner in which the distillation is conducted and the quantity of lime that is added. *The lime acts chemically, seeing that it produces green colorations which do not occur in the distillations of rosin without the addition of lime*, but it acts mechanically also, and in a greater degree by dividing the molecules of the material to be distilled. The lime has also the advantage of neutralizing the rosin acids, which, although weak, exist in rosin oils just as free fatty acid in vegetable oils, and may likewise be detected in them by litmus paper.

Greater fluidity is got in the oils by numerous means; first of all by augmenting the proportion of lime, but this lessens the proportion of blonde and white oils obtained, and these are the most valuable. The quantity of blue and green oils called "low products" increases at the expense of the white and blonde. The oils can also be rectified by a second or third distillation, and still lighter oils are obtained at each operation, which the pitch left at the bottom of the vessel after each operation easily explains.

It has been seen that the oils distilled over when lime is added assume different colours at various periods of the distillation. Blonde at first, they turn white, then blonde again, then blue and green. Nevertheless, to obtain these different colours pale rosins must be used; with black rosins the tints have a tendency to darken, and not even the white oil is obtained. Each of these colours is in request in commerce for some particular use or other. *The makers of printing inks require very fluid oils without viscosity and a limpid white or blonde. They must have a density approaching as nearly as possible that of linseed oil, with which they are mixed*, or for which they are substituted in the manufacture of printing inks. The oil merchants who use rosin oils, to make mixtures with mineral or vegetable oils require the oil to be of a colour and density approaching as nearly as possible that of the oil with which they want to make a mixture. The French railway companies, who make a mixture of

equal proportions of colza and rosin oil for wagon grease, choose the blonde because it is the same colour as colza, and they also exact a particular density. It must be fluid in order to travel quickly by capillarity through the wick of cotton by which it communicates with the axles.

The manufacturers of grease take the colour which they wish to give to their grease—green, blue, or blonde; and white when they want to get a grease of a fancy shade—rose, violet, or chocolate, for instance, tints which they obtain by mixing colouring matters in powder or in solution with their white oil. The mine owners, who use rosin oil to lubricate their wagons, are indifferent about the colour, and content themselves with the blue or green oils, but they want them strong and thick, or light and fluid, according to the kind of machine to be lubricated, and according as to whether the oil is directly dropped on to the bearing, in which case it must be adherent and viscous, or whether it has to be shut in a box, from which it can escape drop by drop over the axle, in which case it must be very light and as free from carbon as possible, in order not to foul the axle. But all these users want an oil as limpid as possible, translucid and not opaque, and free from that unequal appearance which shows that mucilage and water have been carried over with it in the process of "distillation". To meet the requirements of the purpose to which the rosin oil is to be applied, the rosin oil distiller must know the exact time to cut his still for that particular purpose.

Distillation under Pressure of Turpentine, Rosin, Rosin Spirit, and Rosin Oil.—Turpentine oleo-resin, spirits of turpentine, rosin, rosin spirit, and rosin oils (blonde, blue, and green) have been distilled under pressure with results of high practical value. Turpentine oleo-resin distilled under 2 to 4 atmospheres pressure gives, in the first place, a turpentine oil of much lower density than otherwise attainable, the total product—which is some 5 to 6 per cent greater than from ordinary distillation—forming, when mixed, a normal turpentine oil of specific gravity 0·860/62. In this case the use of direct steam is advisable, although indirect steam, gradually heated to 200° C., answers very well. A tubular condenser can be used with advantage, and the increased yield shows the practical benefit of the method. On the other hand, sundry experimental distillations and rectifications of turpentine oil under a few atmospheres pressure led to no results capable of utilization in practice, the product, though specifically lighter and of milder odour, being in point of solvent power and other qualitative properties in no way superior to ordinary turpentine oil. Probably, however, further strictly theoretical labours in this connexion may lead to new and scientifically valuable issues, since the extremely fine essences—recalling various fruity ethers—obtained in the fractionation of the first runnings have not, so far, been more minutely investigated, and are, therefore, full of interest to the scientist. These remarks apply equally to the essences obtained from the tar deposited when this turpentine oil is washed with soda lye.

The attempts made to distil rosin under pressure have not hitherto proved satisfactory, owing to the troublesome and protracted labour required, the use of direct steam being precluded. It is true that a much larger yield of good rosin spirit and rosin oil can be produced, but this object is attainable by simpler means, and consequently the application of this method to that purpose need not be further discussed.

More advantageous is its employment in the distillation of rosin spirit and rosin oils, in both of which cases it is certain to prove beneficial and profitable, at least in large works. In the ordinary methods of rectification applied to crude rosin spirit, to fit it for working up to turpentine oil, only about 50 per cent of workable spirit is recovered, together with a light rosin oil of inferior quality ; whereas by distillation under 3 to 4 atmospheres, at least 80 per cent of suitable rosin spirit can be recovered. Moreover, up to 20 per cent can be recovered from the blonde rosin oil, 5 per cent from the blue oil, and about 10 per cent from the green oil, a total—including the pinolin already mentioned—of about 38 per cent. The rosin oils thus prepared from the blonde and blue oils are light, very pale in colour, and of extremely mild odour, and consequently in good request for numerous purposes, the green oil yielding, without any further distillation, a thick, quick-drying oil, principally useful for the manufacture of carbolineum.

In another branch various wood-tar oils from a cellulose factory employing pine, and a Finland wood-tar oil, may be distilled under a pressure of 4 to 9 atmospheres, with the object of increasing the yield of light oil. (The increased yield of spirit is all through due to "cracking".)

CHAPTER XI.

ROSIN SPIRIT—ROSIN OIL.

Rosin Spirit.—The German "pinolin," the French "essence vive de resine," is used abroad for cleaning machinery, when refined with sulphuric acid and soda, and redistilled it is used to adulterate spirits of turpentine. Crude unrectified rosin spirit has a not over-pleasant smell, dark port wine to claret colour, and a decided blue fluorescence, so that it can only be used in the making of black and white ships' varnish. It finds a use in the making of wagon grease. It abounds in rosin acids carried over vesicularly. These acids form rosinates of lime with the lime water, and being insoluble in the latter liquid they separate out in the form of a curd. When say 5 per cent or less of this curd is churned with rosin oil, it forms with it a semi-solution or emulsion which soon solidifies into a more or less consistent lubricant. It is incorrect to say that the lime combines with the rosin oil hydrocarbide up to $(C_{10}H_{16})^{13}CaO$. Lime no more combines with neutral unresinified rosin oil than it does with neutral mineral oil. If the above lime rosinate compound be dissolved in mineral oil a similar grease will be formed.

Rectification.—The crude rosin spirit is simply redistilled over a naked fire with the aid of finely divided steam and with or without the addition of 3 to 5 per cent of powdered lime and of ½ per cent of soda lye. It is, however, far better to redistil it *in vacuo* by direct or indirect steam and a double discharge condenser, by the use, in fact, of plant specially constructed for the purpose. Pale spirit free from rosin acids and rosin oil and of a pleasant mild aroma is thus obtained. Such a spirit commands a higher price in the market, besides there is an increased yield of 5·7 per cent more than in the ordinary precarious rectification over a naked fire. The residual light rosin oil left from several rectifications of rosin spirit is generally separated in a still by direct fire. A more rational method is as follows: The crude rosin spirit of density 0·855 to 0·900 is best treated (washed) by direct steam in a tank at 80° to 100° (176° to 212° F.) with 3 to 3½ per cent soda lye of 36° to 40° Baume (66·4° to 76° Tw.), say 4 to 5 lb. of 77 per cent caustic soda *in* 1 gallon, i.e. about equal parts of caustic soda and water by weight. After an hour's treatment the lye is run off and the oil again washed with tepid water. After running off the wash water it is mixed with 2 per cent of concentrated sulphuric acid

(168° Tw.) at a low temperature, 15° to 25° C. (59° to 77° F.), in another vessel fitted with a mechanical or an air agitator. After allowing the acid to settle out, which takes place in about three or four hours, it is again washed with 2 per cent of soda by direct steam so as to neutralize the product completely. It is finally rectified *in vacuo* by direct and indirect steam after admixture with ½ per cent soda lye and 3 to 5 per cent of lime water. The now perfectly limpid rosin spirit has a pleasant but characteristic mild aroma, which it is said may be improved by the addition of charcoal during distillation. It is now identical in gravity with spirits of turpentine and similar in properties. The gravity of 0·860 to 0·865 is easily maintained. It is claimed therefore that it can after this treatment be used either alone as a substitute for spirits of turpentine or in admixture with it. To render this rosin spirit admixture more similar to commercial spirits of turpentine, it may be mixed prior to rectification with a few per cents of the essential oil distilled from pine stumps, etc.

Rosin Oil.—According to Renard rosin oil consists of :—

TABLE XLIX.—COMPOSITION OF ROSIN OIL.

	Density.	Per cent.
1. Diterebenthyle $C_{10}H_{15}$, boiling-point 333°-336° C. .	0·9688	80
2. Diterebenthylene $C_{10}H_{14}$, boiling-point 345°-350° C.	0·989	10
3. Didecene $C_{20}H_{36}$, boiling-point 330°-335° C. . .	0·936	10
		100

(1) *Diterebenthyle* $C_{10}H_{15}$ is a colourless oil, boiling at 333° to 336° C., and of density 0·9688 at 18° C., rotating the planes of polarized light 0·590 to the right (dextro-rotatory). Its index of refraction is 1·53. In a thin layer it absorbs 10 per cent of oxygen from the air. Concentrated sulphuric acid converts it into a sulphuric derivative. It is attacked by chromic acid, nitric acid, and bromine, like the terpene hydrocarbons. (2) *Diterebenthylene* $C_{10}H_{14}$ is a thick colourless oil, slightly fluorescent, boiling at 345° to 350° C. Its density is 0·9821 at 120° C. It is dextro-rotatory (+ 4°). It does not change on exposure to the air, and neither sulphuric nor hydrochloric acid have any action upon it. (3) *Didecene* $C_{20}H_{36}$ is a colourless, non-fluorescent oil, boiling at 330° to 335° C., and possessing a density of 0·9362 at + 12° C. It is levo-rotatory (− 2°). It does not change on exposure to the air, and neither sulphuric nor nitric acid have any action upon it.

Sulphuric Acid Spot Test.—One drop spotted on ten of oil gives a brownish-red nucleus, quickly passing to black. This test is so delicate that it allows a minute quantity (1 or 2 per cent) to be detected in linseed oil. It is a waste of time and dear chemicals to apply any of the numerous modifications of Liebermann's test. The density of rosin oil is comparatively high, as shown in Tables XL, XLI, XLIII, XLIV, XLIX, L.

TABLE L.—PHYSICAL PROPERTIES OF THE VARIOUS OILS FROM THE DRY DISTILLATION OF ROSIN.

Description of Oil.	Average Density at 15° C.	Co-efficient of Expansion.	Density at 15° C. in Relation to Density at t°.
Pale oil, first distillation	0·9823	0·000663	0·00064t
Pale oil rectified by second distillation	0·9712	0·000673	0·00065
Blue oil	0·9810	0·000717	0·00070
Green oil	0·9901	0·000660	0·00065
Spirits of turpentine	0·8690	0·000918	0·000789

Rosin oil is insoluble in water and in ethylic alcohol. On boiling with a large excess of 95 per cent alcohol, rosin oil is slightly soluble, but the dissolved oil settles out on cooling. Rosin oil is not saponifiable, but in distilling it carries unchanged rosin over in its train which renders it acid. Rosin oil containing entrained rosin thus yields, with alkalis, rosin soaps, imparting a milky aspect to the oil. These oils consist essentially of hydrocarbides and can in no way be compared with fatty oils. The rosin oil from the middle runnings has several defects which depreciate its market value. It is cloudy, more or less dark coloured, acid, has an empyreumatic smell, a fluorescent reflex (bloom), and great viscosity. To remove or mitigate these defects the oil is refined.

Leaving the naturally fluorescent bluish-greenish-brown colour of crude rosin out of account for the moment, it is to be observed that its dull, cloudy nature is due to the presence of small quantities of organically derived water formed during and as a result of the destructive distillation of the rosin or as a result of a saponification of a part of the rosin being distilled by the lime used in the fire (see Equation, p. 131). This organically derived water distils over with the hydrocarbide vapours which the oil retains in the form of highly comminuted globules constituting an emulsion. These water globules may be removed by heating the oil, and if, during heating, air be injected, the exit of the steam from this organically derived water is facilitated. The operation is performed in, say, a 220 gallon tank, fitted with a steam coil and air injector. This heating, however, darkens the oil, but possibly this is due to a certain extent to the fact that water-freed oil, of whatever nature, is always much darker in colour than the water-logged oil, or emulsion, from which it is derived. Neither does heating with injection of air completely remove the smell. Again, if the operation be conducted at a higher temperature than 110° to 120° C. (230 to 245), the viscosity of the oil is much increased, and, possibly, its acidity. In regard to the sun-bleaching method, proposed by Dorian twenty years ago, viz. to let the rosin oils to be refined stand in wide tanks, exposed to the sun under glass roofs. There are the same objections to this method as to the sun-bleaching

of linseed oil (see Vol. I, pp. 17-18); moreover, rosin oil does not lend itself so kindly to sun-bleaching as linseed oil. Therefore the sun-bleaching of rosin oil is in Britain less practised than that of linseed oil. Rosin oil may be rectified by potters' clay. The clay is purified, sifted, and dried at 300° C. (572° F.) in a suitable vessel and sifted hot on to the surface of the oil. Fullers' earth might also

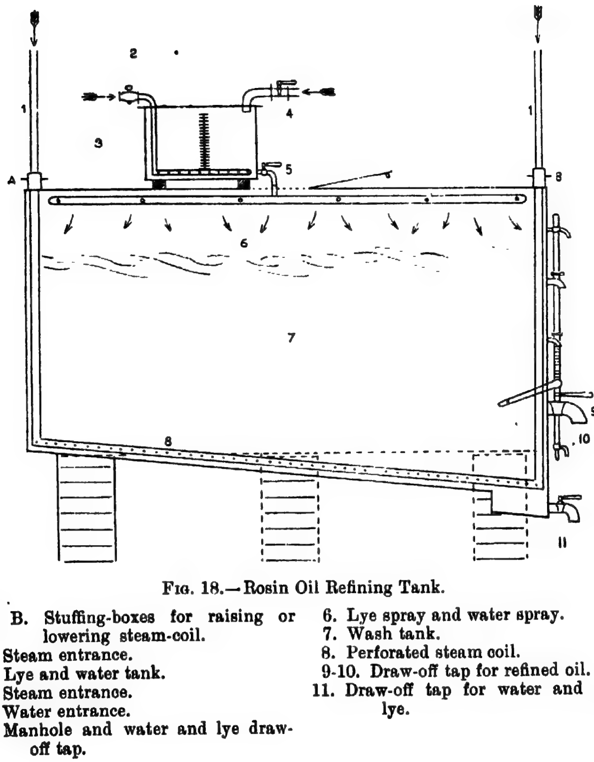


FIG. 18.—Rosin Oil Refining Tank.

A, B. Stuffing-boxes for raising or lowering steam-coil.
1. Steam entrance.
2. Lye and water tank.
3. Steam entrance.
4. Water entrance.
5. Manhole and water and lye draw-off tap.
6. Lye spray and water spray.
7. Wash tank.
8. Perforated steam coil.
9-10. Draw-off tap for refined oil.
11. Draw-off tap for water and spent lye.

act efficiently. At the same time the oil is slightly bleached; 1 to 2 per cent of clay gives good results. The oily mud should be run into tanks to deposit or passed through a filter press. Other dehydrating agents give good results, sodium, fused calcium chloride, etc.

Refining Rosin Oil: German Process.—The apparatus consists of a washing tank (Figs. 18-20) 10 feet by 5 feet by 5 feet, and a bleaching tank (Fig. 21) of similar size. Five tons of blonde oil are placed in the former to allow the acetic acid water to settle; about four parts of hot water are added, and the whole boiled by *direct* steam. When freed

from acid water the oil is again boiled by *direct* steam, and treated with 4 to 5½ per cent of soda lye of 36° to 40° B., specific gravity 1·332-1·383, sprinkled over the surface, the heating being continued until a sample

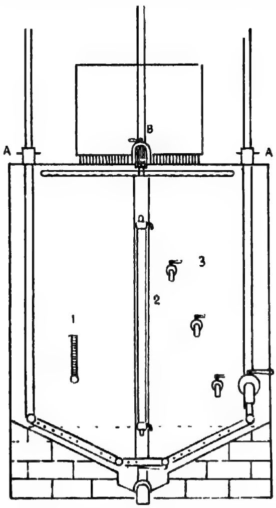


FIG. 19.—Rosin Oil Refining Tank.
1. Thermometer. 3. Draw-off taps for test-samples.
2. Oil-gauge.

shows the oil to be free from rosin and acid, whereupon the steam must be instantly shut off or the product will assume a dark colour and turbidity due to dissolved rosin soaps; the steam coil should then be at

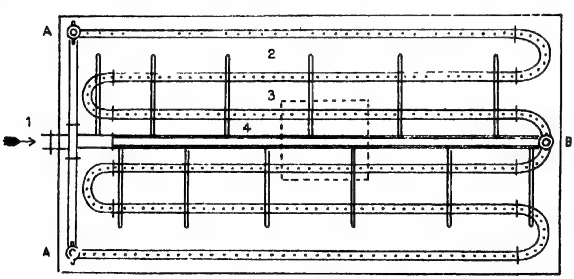


FIG. 20.—Rosin Oil Refining Tank.
1. Steam entrance. 3. Ground plan.
2. Steam coil. 4. Water and spent lye exit.

once lifted out of the liquid. Immediately after the steam is shut off, the steam coil, with its attached feed pipes, is lifted up out of the oil by means of the stuffing-box arrangement in the head of the vessel,

and is cleared of liquid by a momentary blast of steam. An improvement due to Boleg, which will be appreciated by practical men, entirely obviating the cleansing of the coil after alkali washing, and before the after-washing is begun, a drawback hitherto incidental to the refining of rosin oil, whether the washing was effected in similar

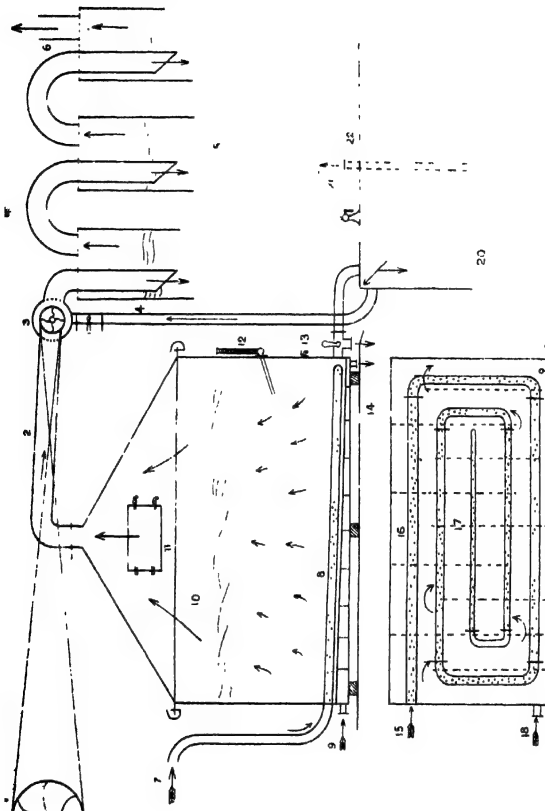


FIG. 21.—Rosin Oil Oxidation or Bleaching Tank.

1. Belt and pulley (shafting).
2. Oil vapour exit.
3. Fan.
4. Removal of oil vapour.
5. Condensation of oil vapour.
6. Gas exit.
7, 15. Air pipe.
8, 16. Air agitator.
9, 18. Steam entrance.
10. Oxidation and bleaching vessel.
11. Manhole.
12. Thermometer.
13. Test sampling tap.
14, 19. Steam exit.
17. Ground plan.
20. Cooler and store tank.
21. Air tap.
22. Discharge pipe.

vessels or in those fitted with agitators, viz. that as small quantities of rosin soaps adhered to the stirrers or the coil, the oil was always, to some extent, contaminated and darkened in colour, and frequently rendered persistently turbid during the subsequent washing with water, to avoid which the only feasible method was the tedious plan of having a separate washing tank for the second operation. The new appliance saves the loss of time in transferring from one vessel to

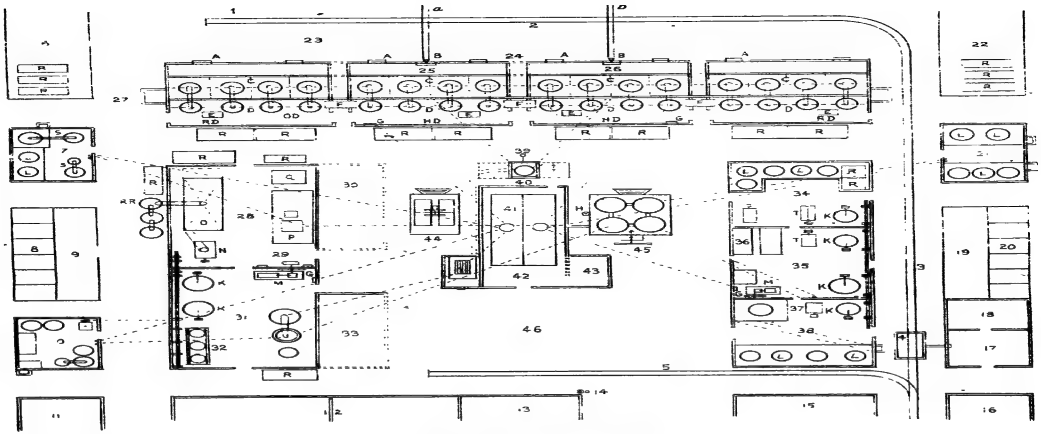


FIG. 22 — German Rosin Distillery.

A. Fire doors for stoking.
B. Spot from which stills are charged from trucks.
C. Stills.
D. Condensors.
E. Vacuum pumps.
F. Rosin gas apparatus.
G. Steam distributor.
H. Pulsometers.
HD. Rosin stills.
I. Printed as T.
K. Agitator.
L. Open boiler (rosinates, etc.).
M. Engine.
O. Oxidation apparatus.
OD. Crude rosin oil stills.
P. Washing apparatus.
Q. Rosin lye tank.
R. Coolers or store tanks.
RD. Rosin residue stills.
S. Rosinates and paint oil vessels closed.
T. Roller mill.

0. Laboratory.
1. Rosin warehouse.
2. Tramway.
3. Tramway.
4. Weighing machine.
5. Tramway.
6. Oil store.
7. Rosinate and boiled oil factory.
8. Tanks.
9. Store.
11. Stable.
12. Office.
13. Gate house.
14. Arc lamp.
15. Dispatch.
16. Cooperage.
17. Weighing packing room.
18. Material store.
19. Store.
20. Tanks store.
21. Oil and grease boiling house.
22. Oil store.
23. Coal store.
24. Distillery.

25, 26. Fires.
27. Chimney.
28. Oil refinery.
29. Dynamo.
30. Adjunct for second refining.
31. Oil products department.
32. Colour mills.
33. Adjunct for second refining.
34. Wagon grease factory.
35. Machinery oil and grease factory.
36. Workshop.
37. Weighing machine.
38. Pitch factory.
39. Arc camp chimney stalk.
40. Workmen's bath room.
41. Steam boilers.
42. Superheater.
43. Smithy.
44. Vacuum apparatus for oil conveyance.
45. Fan.
46. Coal store.
a, *b*. Tramways.

[SPIRIT VARNISHES. *To face p.* 144.

another, and the cost of a second tank, besides yielding a much cleaner, paler, and always bright oil. After leaving the whole at rest for about an hour to enable the lye to subside, it is drawn off into a vessel until pure oil begins to run out of the tap. The steam coil is then lowered again and direct steam passed gradually, and carefully, into the oil, warm 50° to 60° C. (122° to 140° F.) water, to the extent of about one-third the volume of oil present, being at the same time run in from the lye and water tank. Here again care is necessary not to boil the mixture too violently or too long, a temperature of 105° C. (221° F.) being the maximum, and the operation continuing only until a test sample shows that the water (like the lye in the former washing) settles down quickly and leaves the oil clear. With accurate working the water will subside completely within the hour, and in such event—if, as should be the case, the oil be clear and the washings do not appear too dirty and soapy—no further treatment will be required, and the oil can be drawn off through the upper tap into the bleaching (oxidizing) apparatus. The best results, pale, odourless oils free from resins and acids, are got thus: The oil, occupying a depth of 30 to 40 inches in the vessel, and previously warmed by indirect steam to a temperature of about 60° C. (140° F.) is treated for two to three hours with a current of air at 60° to 80° C. (140° to 176° F.) forced in by means of a blower, through a finely perforated coil, the light oil vapours and gases evolved at the surface being drawn off by a fan and discharged through a wide pipe into the condenser—an operation which is indispensable to this process, but which is often erroneously omitted. By increasing steam and air the temperature of the oil is raised to 115° C. (239° F.) in the course of the next hour, and is there maintained for fifteen to (maximum) thirty minutes to remove the fluorescence (bloom) of the oil, which thus loses its bluish cast, whilst the evolved vapours acquire a peculiar, pungent, camphor-like odour. The exhaustion of these vapours is continued in the storage and cooling tanks until the temperature of the oil has fallen to about 30° C. (87° F.). This is found to be indispensable for the production of fine, clear, and inodorous oils. Open bleaching pans have proved both troublesome and actually dangerous; but an addition of 10 to 15 per cent of brine to the oil—the water lost by evaporation being replaced by hot water either every half-hour or twice during the final hour—prevents the renewed formation of oxidation and empyreumatic resins, and absorbs the substances which would go to form these resins, its colour being thereby changed to brown though it separates out easily. The now-finished oil is free from rosin and acids, so that, unlike oils bleached by other methods, it no longer reacts with caustic soda. This, Boleg claims, is the sole method yielding rosin oils drying without cracking or tackiness, and suitable for boiled oil and varnish-making. The same method as for *crude blonde oil* is employed in working up *rectified or double distilled blonde oil* for special purposes, e.g. lubricating oil, the vapours being continuously drawn off and salt water added,

the only differences being that $1\frac{1}{2}$ to 2 per cent less caustic soda lye (i.e. only 3 to $3\frac{1}{2}$ per cent) is needed, and that the temperature of the oil at the close of the bleaching process is not allowed to rise above 105° C. (239° F.). For *refining blue oil* the same method is pursued, 3 to 4 per cent of lye being used; but to obtain a clear, transparent product, not too deep red in colour, the oil should be treated, or at least washed, *while fresh from the still, and worked up immediately after rectifying.* A fine orange-yellow to pale red oil, suitable for many purposes, is thus produced. The practice of employing sulphuric acid to make the oil water-white is to be condemned, a better result being attainable by the addition of quicklime or caustic soda, and animal or wood charcoal to the oil during the rectification *in vacuo*, time and expense being also saved. The oils prepared as above being free from acids and rosin, and having exceedingly mild aroma, are far more suitable for their various uses than common oils and can thus be utilized to better advantage. The various grades can be employed, according to quality, for making paint, printers' ink, lubricating oil, preparations for boring and planing tools, polishes, woodwork, leather work, as preservatives, for making carbolineum, artificial train oil and dégras, in the linoleum, insulating material, soap and perfumery industries, and for medicinal purposes.

Refining Rosin Oil: French Methods.—Several processes are in vogue: (1) The simplest is to age the oil, that is to say, allow it to settle for a long time in capacious tanks, and to let it clarify spontaneously by deposition. The water and other impurities settle out, and the clarified oil can then be decanted, or run off from above. But such a process is both costly and tedious, entailing costly plant and much space. (2) The oil is heated in copper pans either over the open fire or by a steam jacket. The oil loses its viscous nature rapidly on heating, much quicker, indeed, than one would naturally imagine. The oil having thus been converted into a mobile liquid by heat, the path is open for the impurities to settle out, but the colour darkens rapidly in the process, or is thought so to do. But an emulsion, or an oil containing much diffused water, is always paler than the same oil free from water. (3) Some rosin oil refiners treat the oil by sulphuric acid, as in Thenard's process for refining linseed oil (Vol. I, pp. 15-16). The sulphuric acid chars the resinous matter, but it is difficult to wash the oil free from acid, even after treatment with soda and redistillation. The sulphuric acid splits the oil up into two portions. One portion, the main bulk of the oil, is insoluble in the acid, and when washed with soda and rectified furnishes an oil only very slightly attacked by the oxygen of the air, and perfectly resistant to sulphuric acid. The other portion is soluble in sulphuric acid, from which it separates out, on the addition of water, and resinifies very quickly in the air by absorption of oxygen. Sometimes the rosin oil is purified by redistilling it, but this entails a loss of 6 to 8 per cent, part of which is rosin spirit collected apart.

4. *Bleaching Rosin Oil by Sunlight.*—The regular and strong heat of the southern sun projected on the surface of a tank filled with rosin oil quickly precipitates the resinous matter and water to the bottom and the clear pale oil floats to the surface. Capacious shallow tanks are covered with glass frames, filled with rosin oil, and exposed to the sun, which is said to bleach the oil in a few days. To deodorize and de-bloom and to free it from vesicular rosin, the oil to be purified is mixed with soda lye, and constantly stirred by a mechanical agitator, in a semi-cylindrical open pan, heated to 120° C. (248° F.) on the open fire or by an open steam coil. In the latter case agitation may be dispensed with. The soda saponifies and dissolves the rosin, water is then added, and the heat brought to 40° to 50° C. (104° to 122° F.) and the whole allowed to settle. The oil is then siphoned off, washed again with hot water, and exposed to the air in capacious shallow tanks. It is kept at a temperature of 50° to 70° C. (122° to 158° F.), and after a few days the oil is de-bloomed and deodorized. The decanted oil is then perfectly pale, odourless, and will not resinify. It is also free from the entrained rosin acids, which have been neutralized by the caustic soda.

5. *Siccative Rosin Oil.*—When required for paint purposes a siccative rosin oil may be made as follows: (1) Agitate the oil with 2 per cent sulphuric acid in a lead-lined tank. (2) Wash with boiling water in a current of steam. (3) Macerate the oil for two hours over pulverized quicklime. (4) Distil the oil over same quicklime. (5) Wash with boiling water in a current of steam. (6) Boil for two hours with 8 per cent of dry white lead.

The oil becomes siccative. It is left to settle and then exposed to sunlight to bleach it.

6. *Oxidation of Rosin Oil. Boiling of Paint Oil.*—This is best done in a cylindrical vessel with a conical bottom and a jacket for heating with steam. The oil having been heated in the vessel to 100° to 110° C. air is blown through the oil. This at first brings the temperature down slowly to about 90° C., but it then rises again. When it has reached 130° C. both steam and air are shut off, and the apparatus is cooled to 110° by passing cold water through the jacket. The steaming and blasting are then repeated once more. When the operation is over, the oil has lost the characteristic features of rosin oil, and has a pale brown colour. It has also thickened considerably, and has acquired an agreeable smell, like that of molasses. If pale yellow oil is wanted, the resin oil must undergo a further distillation before oxidation. but the remainder of the process is as above. If these prepared rosin oils are painted on a plate of glass side by side with boiled oil, they both dry in about the same time, with a slight advantage in favour of the linseed oil. The dry coat from the rosin oil is very hard and brilliant, will not crack, and resists weather well. Six months' ordinary exposure has no effect on it. The rosin oil product is improved by the addition of 10 per cent of oil of turpentine or 20 per cent of good boiled oil.

Deblooming.—Rosin oils are naturally differentiated from all fixed vegetable and animal oils by their characteristic blue or green fluorescence. Mineral oils exhibit a similar fluorescence or "bloom," which is the more common term in the trade. This bloom is easily detected by turning the back to the light in examining the sample, or by spotting the oil on a black background. In blending rosin oil with animal or vegetable oils it is often attempted to eliminate the bloom. This is so far effected by previously treating the rosin oil with nitro-naphthaline, a yellow crystalline body used as a dye-stuff of the formula $C_{10}H_{17}NO_2$. The pulverized nitro-naphthaline is dissolved in a small quantity of oil and added in the proportion of ½ to 2 lb. per cwt. of oil according to the amount of bloom. Nitro-naphthaline renders previously neutral oils slightly acid. Mirbane oil likewise deblooms rosin oil, but the amount of debloomer required in that case renders the process unprofitable. Again, theoretical men point out that diterebenthyle and didecene, the non-fluorescent hydrocarbides, boil at 330° to 335° C. (626° to 635° F.) whilst fluorescent diterebenthylene boils at 345° to 350° C. (653° to 662° F.). By carefully watching the temperature, and cutting the stills at the proper time during rectification it is said non-fluorescent oils may be afterwards selected, but there is a great deal of difference in controlling a gas-heated glass retort and in working a copper or iron still heated over a naked fire. Rosin oil has a very pronounced empyreumatic odour which is even more pronounced in the case of rosin spirit. Regulated heating does not completely deodorize the oil, and washing with, and rectification over, soda lye is necessary to remove the strong-smelling principles. Moreover, very pale almost colourless oils are so obtained. To remove the smell, washing with soda followed by agitation with sulphuric acid is of all processes said to be that which appears to yield the best results, but this method has not been adopted in actual practice, possibly because it is found too costly, the oil requiring to be redistilled after treatment. The process most often adopted is to rectify the oil in stills capable of holding 1½ to 5 tons of oil. Above the body of the still underneath the still-head a basket is hooked on containing soda which falls gradually into the oil as it is dissolved by the vapours on their way to the condenser. It is necessary to apply heat very gradually so that the rectification lasts thirty-six hours. When the oil is hot a current of steam may be carefully applied, but that is a delicate operation. If the water, not converted into steam, accumulates at the bottom of the pan it gives rise to bumping or even explosions. A pyrometer is then indispensable. Nitro-naphthaline imparts to oils deodorized by rectification a slight smell which attenuates any remaining empyreumatic smell. Mirbane oil may mask the smell of rosin oil, which is then replaced by that of bitter almonds. Amylic alcohol added by small portions, from 0·2 to 1 per cent, completely neutralizes the smell of rosin oil. With a slight excess of alcohol the smell of the English bon-bon is got. Blonde amylic

alcohol does well enough for the purpose. It acidifies slightly in the air, but it may be preserved over soda, and there is thus simultaneously obtained an alcoholic soda, by which both the smell and the last trace of acidity are removed from the oil. The deodorization of rosin oil may also be attempted by combining the valeric and butyric acids contained in the oil with ethyl alcohol, but the acid darkens the oil, and the small quantity which combines only yields a faint odour of fruit, but possibly the darkening of the oil is more due to the alcohol removing the emulsion by absorbing the water.

Rosin oil contains acids, which may be subdivided into two groups: (1) In the first group are the volatile acids, acetic, valeric, butyric, which may be eliminated by heating in the open air or by simple rectification. (2) In the second group comes rosin mechanically entrained, bringing resinic acids of which pimaric acid $C_{20}H_{30}O_2$ is typical. To combine these organic acids it is necessary to saponify them, in a rectification still, by washing soda. Until lately caustic soda was used. Carbonated alkali (dry soda ash) may be substituted for caustic soda. Caustic soda is more costly, involves expensive packages, wrought-iron drums instead of bags, is more difficult to handle, and finally, owing to the water which it contains, its neutralizing power is not so far superior to that of soda ash. Theoretically, 53 of dry carbonate, or 40 of caustic soda, suffice to form a neutral rosin soap with 302 parts of pimaric acid. Practically 60 lb. of alkali for 300 lb. of acidity may be taken as the amount required. If the acidity of the oil to be treated be known, the amount of soda to use can easily be determined. The acidity of rosin oil may be determined by alcoholic (amylic) soda. Amylic alcohol is an excellent solvent for the different products present during the test: phenolphthalein, soda, rosin oil, rosin soap.

7. *Preparation of High Grade Rosin Oils.*—To produce high grade oils, it is necessary to select the finest products from the beginning to the end of the operation. First of all, *semi-pale* rosins are preferred to *black* rosins. The slight difference in price is easily regained in the resultant oils. Little lime and slow distillation are essential points, and the middle runnings are freed from the last traces of smell, either in a tank or cylinder or in a deodorizing vessel. The bloom is removed by nitro-naphthaline, and the last traces of smell and acidity with alcoholic (amylic) soda. These high grade oils speedily darken slightly, and perceptibly recover their bloom. Manufacturers accordingly stipulate for a fortnight in which to execute orders, which enables them to dispatch oil recently refined.

8. *Reactions.*—(*a*) Perchloride of tin produces a blood-red coloration, quickly passing to purple. (*b*) Nitric acid attacks warm rosin oil with production of nitrous vapours. The product when thrown into water changes to a yellow waxy mass, is dextro-rotatory (+ 30°) and rarely levo-rotatory (− 8·24°). Mineral oil is without action on polarized light. Although the density always affords sufficient data to

differentiate between mineral oil and rosin oil, we can confirm our inference by (c) the eläidin test (Vol. I, pp. 132-3). In the presence of rosin oil a deep red coloration is produced, whilst mineral oils remain unchanged. (d) Glacial acetic acid dissolves rosin oil, but mineral oil is insoluble in that reagent. (e) The iodine number rarely goes above 14 in mineral oils, whilst it may go as high as 43 to 48 in rosin oils. With shale oil, however, the iodine number may rise to 21. (f) *Storch-Liebermann Test.*—In his work on quinovic acid, Liebermann has shown that a solution of that acid in glacial acetic acid, when treated with a little concentrated sulphuric acid, gives a beautiful red coloration, which is likewise obtained with pimaric and sylvic acids, these acids being present in rosin oil. Storch, "Dingl. Poly. In.," t. 267, p. 28, proposes the Liebermann reaction as a test for rosin oil in oils and fats. If we add a few drops of rosin oil to glacial acetic acid and then one drop of concentrated sulphuric acid we obtain a red-violet coloration, which passes rapidly to brown (see Vol. I, p. 103).

CHAPTER XII.

CHEMISTRY OF THE TERPENES AND CAMPHORS.

Terpenes and Terpene Derivatives and their Use in Varnish-making.—The chief terpene, or rather mixture of *isomeric* terpenes, used in varnish-making forms what is known as spirits of turpentine. The *mixture of isomeric* terpenes, constituting spirits of turpentine, are *natural* products agreeing with each other in having the same centesimal composition, C = 88·2, H = 11·8 per cent, and empirical formula $C_{10}H_{16}$. Many terpenes, however, are synthetic products which may or may not exist in nature. Besides forming spirits of turpentine, the natural terpenes enter into the composition, wholly or partially, of numerous essential oils. Camphene, a solid, is amongst the natural terpenes which can be prepared synthetically. But more often the terpenes are liquids, lighter than water, which rotate the plane of polarization, and most of which exist in both dextro-rotatory and levo-rotatory forms, boil between 150° C. and 200° C., and under the action of heat and reagents become altered in density, boiling-point, rotatory power, and even in chemical composition. The great affinity of terpenes for halogen hydride (HCl, HBr, HI), especially for hydrochloric acid (HCl), results in the formation of a well-defined class of compounds, known, but erroneously so, as artificial camphors. Wallach was the first to examine the terpenes in a systematic manner. He showed that a very large number of the terpenes, known at the date of his researches under different names, and considered as distinct, were identical, e.g. the portions of hesperidene, citrene, oil of bergamotte, carvene, oils of dill, of erigerone, and of pine leaves, boiling between 175° and 176° C.; secondly, the terpenes boiling between 180° and 182° C., cinene, cajeputene, caoutchine (di-isoprene), with the parts of camphor oil boiling at corresponding temperatures, and of that product which is formed by heating all the terpenes hitherto examined to 250° to 270° C. Lastly, he showed that all the hydrocarbides obtained by decomposing terpene di-hydrochloride, by melting at 49° C. to 50° C. with aniline, are identical with these bodies. He left over, for future investigation, in how far the mutually very similar terpenes boiling at 160° C. and occurring in oil of turpentine, oil of pine leaves, of juniper berries, lemons, eucalyptus, mace, dill, sage, were identical, noting, however, that at elevated temperatures they all pass into the same terpene. From these investigations Wallach

TABLE LI.—SHOWING THE CHEMICAL AND PHYSICAL PROPERTIES OF THE TERPENES.

Divalent Terpenes.	Boiling-points, °C.	Densities.	Optical Deviation.	Halogen Derivatives.	Nitrosites, etc.	Hydration Products.
Pinene .	155°-156°	0·8587 at 20°	– 43°·4 + 32°	$C^{10}H^{16}.HCl$ m.-p. 125°	Nitrosochloride m.-p. 102°-103° Nitrosopinene m.-p. 132° Nitrolbenzylamine m.-p. 122°-123°	—
Camphene .	158°-160° (solid m.-p. 50°)	0·850 at 48°	– 80°	$C^{10}H^{16}.HCl$ m.-p. 147°	—	Isoborneol
Fenene .	158°-160°	0·864 at 20°	—	—	—	Isofenolic alcohol m.-p. 61·5°-62°
Tetravalent Terpenes.						
Limonene .	176°	0·8464 at 18°	± 106°·8	$C^{10}H^{16}Br^4$ m.-p. 104°-105°	—	Terpineol
Dipentene .	175°-180°	0·8500 at 15°	—	$C^{10}H^{16}Br^4$ m.-p. 124°-125° $C^{10}H^{16}.2HCl$ m.-p. 50°	—	Terpinol
Terpinolene .	183°-185°	—	—	—	—	—
Terpinene .	179°-181°	—	—	—	Nitrosite m.-p. 155°	—
Sylvestrene .	176°-177°	0·851 at 16°	+ 66°32	$C^{10}H^{16}.2HCl$ m.-p. 72° $C^{10}H^{16}Br^4$ m.-p. 135°-136°	Nitrosochloride m.-p. 106°-107° Nitrolbenzylamine m.-p. 71°-72°	—
Carvestrene .	178°	—	—	$C^{10}H^{16}.2HCl$ m.-p. 52°·5	—	—
Fenelene .	175°-176°	0·842 at 20°	—	—	—	—
Thuyene .	—	—	—	—	—	—
Phellandrene	170°-172°	—	—	—	Nitrite m.-p. 103°-104°	—

formulated a new classification of the terpenes, distinguishing (1) *hemiterpenes* or *pentenes* (C_5H_8), including isoprene and valerylene, and (2) *true* terpenes ($C_{10}H_{16}$). The latter are resolved into several groups, each chemically distinct, and including various members differing, essentially, by their optical behaviour. The general formula of the terpenes corresponds to $(C_5H_8)^n$. When $n = 1$ we get the hemiterpenes, e.g. isoprene, a substance produced in the destructive distillation of spirits of turpentine, and also of both india-rubber and gutta-percha. Isoprene is supposed to change spontaneously into india-rubber. When $n = 2$ we get the terpenes properly so called, $C_{10}H_{16}$. Pure rectified spirits of turpentine consists, wholly and solely, of terpenes properly so called. Its general formula therefore is $C_{10}H_{16}$. Spirits of turpentine being far more widely and abundantly distributed in nature than any other essential oil, it is not surprising that the terpenes properly so called have been longer known and more carefully examined than either the sesqui-terpenes or poly-terpenes. When $n = 3$ we get the sesqui-terpenes $C_{15}H_{24}$, e.g. cadinene (oil of cade), humulene (oil of hops), cubebene (oil of cubebs). When $n = 4$ or 5 (C_5H_8) we get the poly-terpenes, a class of bodies of which little is known. In varnish-making the terpenes proper and their derivatives need alone engage a close examination. The terpenes proper are subdivided into different groups, according to the number of atoms of halogen or molecules of halogen acid they are capable of absorbing.

1. *Divalent Terpenes* absorb one molecule of halogen hydride (HCl, HBr, HI) or two atoms of halogen (Cl_2, Br_2, I_2), e.g. pinene, p. camphene, p. fenene (anise, fennel).

2. *Quadrivalent Terpenes* absorb two molecules of halogen hydride or four atoms of halogen, e.g. *sylvestrene* (Russian turpentine), with an odour of both bergamotte and lemon oil; *limonene*, in three different modifications, levo-rotatory, with the odour of lemons, dextro-rotatory, with the smell of essence of caraway, and in the racemic condition as *dipentene*. Attempts at the synthesis of quadrivalent terpenes have led to the belief that the terpenes of essential oils are derived from alcohols of the fatty series. Other quadrivalent terpenes are terpinolene, terpinene, fenelene, thuyene, and phellandrene.

Hexavalent Terpenes.—These fix three molecules of halogen hydride or six atoms of halogen. One only is known to exist naturally with certainty, viz. myrecene, extracted from essence of myrtle (*Myrica acres*).

Pinene: Physical Constants.—Lævo-pinene: boiling-point 155° to 156°; $[a_D]$ − 40·32° Riban; − 43·4° Flawitsky; D = 0·8767 at 0° C.; 0·8749 at 0° C. Riban; 0·8587 at 20° C. Flawitsky; $[n_D]$ 1·4648 Riban, Gladstone and Dale. *Dextro-pinene:* from Russian turpentine; boiling-point 153° to 156°; D = 0·8764 at 0° C.; 0·860 at 20° C.; $[a_D]$ + 32. Heat diminishes the rotatory power of pinene; that of French spirits of turpentine after being heated for eight hours at 250°

C. is lowered from − 35·4 to − 32·45, and on heating at 360° C. for one and a half hours it is lowered to − 12° C. A similar diminution occurs with American spirits of turpentine, the alteration in both instances being due to the conversion of the pinene into isomeric quadrivalent terpenes. A red heat acts more violently. If pinene be passed through a red-hot tube it is resolved into hydrogen, isoprene, quadrivalent terpenes, benzene, toluene, metaxylene, cymene, naphthalene, phenanthrene. The same result is got at a lower temperature by distilling in the presence of anhydrous zinc, aluminium, or copper chlorides. The structural formula of pinene is given later in this chapter.

Limonene.—Saussure, Dumas, Laurent, and Gerhardt pointed out that essence of lemon consisted principally of a hydrocarbide, the so-called *citrene*, an isomer of spirits of turpentine (boiling-point 173° C.). Wright and Tilden found in essence of orange a terpene (hesperidene). Long previously Warrentrap and Voelckel discovered carvene in essence of caraway (boiling-point 173° C.), also an isomer of spirits of turpentine. These three bodies were only isomers of one and the same chemical compound, *limonene*, which exists in three forms, lævo, dextro, and inactive. (1) Dextro-limonene occurs in essence of lemons, orange, caraway, bergamotte, and several others. (2) Lævo-limonene occurs in spirits of turpentine from pine needles and in Russian peppermint. (3) Inactive limonene (dipentene) occurs in camphor oil, Russian or Swedish spirits of turpentine, in pine needles spirits of turpentine, bergamotte, oil of cubebs, olibanum, mace, fennel, etc. Lævo-limonene is prepared by fractionation of the essential oils of which it is a constituent, more especially Russian spirits of turpentine (from *Pinus sylvestris*), in which it occurs with lævo-pinene and sylvestrene. It agrees in properties with the dextro variety almost to the degree of optical activity, boiling-point 175° to 176°, D = 0·846 at 20° C., and a rotatory power in alcoholic solution of 6·126 per cent of $[a_D]$ − 105°, and a molecular refraction of 45·23. Limonene monohydrochloride.—If well-dried HCl gas be passed through limonene in CS_2 a monohydrochloride is obtained, boiling-point 97° to 98° C. under 11-12 millimetres. The specific gravity of the lævo-limonene variety is 0·983 at 16° C. (Wallach), whilst that from dextro-limonene was 0·973 at 17·8° C. Both are active and of the same sign as the terpene and equal to − 39·5° and + 40°.

Dipentene.—Dipentene, cinene, inactive limonene, is racemic limonene. It occurs in oil of camphor, Russian and Swedish spirits of turpentine, pine needle oil, bergamotte oil, fennel oil, etc.; it readily forms a di-hydrochloride with HCl and a crystalline compound with bromine. It is a product of several reactions. Dipentene is prepared by heating limonene, and synthetically (Bouchardat) from isoprene. Dipentene may be prepared by the abstraction of 2HCl from its di-hydrochloride, but the product is mixed with cymene, terpinolene, etc. It is better to start from crystallized

terpineol. This alcohol, corresponding to dipentene, yields it on dehydration. Two parts of terpineol are heated with 2 parts of $KHSO_4$ to 180° to 190° C. when $C_{10}H_{18}O - H_2O = C_{10}H_{16}$. Dipentene is inactive. Its boiling-point varies with its purity from 174·5° C. under 731 millimetres to 181-12° C. [? at 760 millimetres]; also its density from 0 850 at 15° C. to 0·8238 at 50° C. Its index of refraction is $n_D = 1{\cdot}47308$. Heat polymerizes it. Heated in alcoholic solution with sulphuric acid it is resinified and converted into terpinene. Alcoholic HCl acts similarly, which explains how mineral acids act on terpene to yield terpinene. Dipentene is first produced and then isomerized into terpinene. Dehydrated by phosphoric acid, dipentene yields cymene $C_{10}H_{24}$. By an analogous reaction fuming sulphuric acid converts it by dehydration and subsequent sulphonation into cymene sulphonate. It absorbs oxygen in the light. Alcohol and nitric acid convert it into terpene hydrate $C_{10}H_{18}O$.

Dipentene Hydrochlorides.—The monohydrochloride $C_{10}H_{16}HCl$ is formed when cold dry HCl gas acts on dipentene. Bouchardat prepared the impure compound from isoprene, and Riban from his isoterebenthene. Dipentene di-hydrochloride is formed when moist HCl acts on limonenes or dipentenes. It was obtained long ago by St. Clair Deville by acting with HCl gas or its solution on terpene hydrate; by Oppenheim by aid of PCl_3 or PCl_5; by St. Clair Deville and Tilden from terpineol and HCl; and by Berthelot by acting on a mixture of spirits of turpentine and alcohol, ether or acetic acid by HCl. It is also formed by action of HCl gas on cineol. Dipentene di-hydrochloride is prepared by the action of HCl gas on an ethereal solution of pinene, or better, of limonene (Wallach), dissolving the latter in half its volume of glacial acetic acid and passing a rapid current of HCl gas whilst the liquid is kept agitated. After some time the mass is run into water, the precipitate is dissolved in a gentle heat in alcohol and precipitated by water. By repeating this operation several times the pure di-hydrochloride is obtained. It melts at 50° C. and boils at 118° to 120° C. It crystallizes in rhombic tables. It is very soluble in warm alcohol, ether, chloroform, benzene, and acetic acid. It has a peculiar reaction. Heated with a concentrated solution of Fe_2Cl_6 it develops a rose coloration turning first violet and then blue. Treated with aniline, dipentene is reproduced.

Sylvestrene.—Discovered (*a*) by Attberg in Swedish spirits of turpentine (*Pinus sylvestris*), in which it is associated with limonene; (*b*) by Wallach and Tilden in Russian spirits of turpentine, of which it is the principal constituent; (*c*) by Aschan, Hjelt, Bertram and Walbaum in the essential oils distilled from coniferous wood or from cones. Such oils also contain borneol esters, their chief constituents. To extract sylvestrene from Swedish spirits of turpentine the latter is treated with potash to free it from phenols and rosin acids, after which it is rectified and the 174° to 178° C. fraction converted into di-hydrochloride by the method given below.

Aniline may be used to regenerate the terpene from the di-hydrochloride, or 1 part of fused sodium acetate and 2 parts of glacial acetic acid, heating for half an hour with a reflux condenser. When the terpene is precipitated by an excess of water, the oil is decanted and distilled by entrainment in an atmosphere of steam. The essential oil distillate is then heated for some time with potash lye and again distilled in an atmosphere of steam. Sylvestrene is comparatively stable under the action of heat. Prolonged heating induces polymerization, but not isomerization. An alcoholic solution of sulphuric acid rapidly resinifies it. Both sylvestrene and carvestrene yield the following colour reaction: When a drop of sulphuric or nitric acid is added to their acetic acid solution an intense blue colour is produced. Other terpenes similarly treated yield red colorations, except pinene and camphene, which give a yellow tint. To obtain this coloration the sylvestrene must be pure or contain but a slight admixture with other terpenes.

Chemical and Physical Constants.—Specific gravity, 0·846 at 20° C., 0·851 at 15° C.; boiling-point, 176° to 177° C. It is dextro-rotatory. Its rotatory power in chloroformic solution 14·316 per cent is $[a_D]$ 66·32, its index of refraction is 1·47468 (Wallach). Attberg found the product extracted by simple fractionation to have a density of 0·861-2 at 16° $[a_D] = +19{\cdot}5°$. Unlike pinene its monohydrochloride is liquid. Its di-hydrochloride $C_{10}H_{16}2HCl$ is isomeric with dipentene di-hydrochloride. Exposed to air and sunlight it oxidizes more rapidly than pinene. Neither its levo-rotatory isomer nor any inactive varieties have been discovered.

Sylvestrene Di-hydrochloride ($2C_{10}H_{16}HCl$).—Sylvestrene di-hydrochloride is the compound from which sylvestrene is prepared. Attberg obtained it by passing HCl gas into an ethereal solution of the terpene. Wallach prepared it in considerable quantity. The Russian spirit after treatment by potash is fractionated. The 174° to 178° C. fraction, a mixture of sylvestrene and limonene, is dissolved in its volume of ether and saturated with dry HCl gas. After two days' contact the ether is evaporated and the residue well cooled, which cannot very well be done except in winter. Crystals of dipentene di-hydrochloride are deposited very soluble in the mother-liquor. They are extracted and dried on a porous plate. The two compounds are partially separated by crystallization in alcohol which yields a mixture rich in sylvestrene di-hydrochloride. Purification is completed by fractional distillation from ether until a melting-point of 72° C. is attained. Sylvestrene di-hydrochloride is easily prepared by saturating the pure terpene with well-dried HCl or a mixture of an acetic acid solution of the terpene and HCl gas, afterwards precipitating with water. Sylvestrene di-hydrochloride forms clino-rhombic crystals, melting-point 72° to 73° C. It is much less soluble in alcohol, ether, and petroleum spirit than dipentene di-hydrochloride. It is dexto-rotatory in chloroformic solution $[a_D] + 18{\cdot}9°$.

Reaction.—Heated with glacial acetic acid and fused sodium acetate or with aniline it yields sylvestrene.

Artificial Camphor.—The product erroneously known under this name since first discovered by Kindt in 1803 is in reality a solid hydrochloride of pinene, viz. $C_{10}H_{16}HCl$, formed by slowly passing dry HCl gas through spirits of turpentine. Different authorities prescribe different temperatures, but owing to the heat developed by the reaction it is difficult to work at a constant temperature, as the too energetic passing of the gas from the generating vessel may suddenly produce so much heat in the absorption vessel that the right temperature is exceeded before it can possibly be cooled down; and if the operations be conducted in glass vessels if cooled too rapidly there is risk of breaking them. Some suggest that the turpentine should be kept cooled by ice during the whole passage of the gas to keep down the temperature which would otherwise increase so as to prevent the absorption of the gas. When the spirits of turpentine is saturated and absorption no longer occurs, and when samples taken from the absorption vessel solidify *en bloc* on being cooled in cold water, the now semi-solid mass in the absorption vessel is set aside in a cool place, when as it cools it becomes a mass of solid crystals embedded in a dark brown fuming liquid. The ratio of the crystals to liquor varies much according to the care taken, the time occupied in absorption, the amount of acid gas passed through, and the regularity and continuance of the same. It will take at least seventy-two hours to saturate 10 gallons, and the expenditure in sulphuric acid and salt is heavy. Instead of first separating the liquid from the solid portion the writer (J. G. McIntosh) distils the two together over soda lye and separates the liquid from the solid distillate by filtration pressure or centrifugal action. The bulk of the chlorine is thus separated, and the snow-white crystalline product can then be used as it is or converted into perfectly pure camphene, and from that into isoborneol, and that again into camphor. The liquid is a valuable perfume and solvent.

Dumas, Berthelot, Riban, and others investigated the process of making "artificial" camphor. But "artificial" camphor is not the sole product of the reaction. The acid as it is fixed by the double pinene bond or link isomerizes the pinene into a quadrivalent terpene; a certain amount of dipentene di-hydrochloride is thus formed along with the solid pinene hydrochloride, and to a greater extent the higher the temperature has been allowed to rise during the reaction. This explains the existence of Deville's terebenthene monohydrochloride. It is also dipentene di-hydrochloride which has been described as terebenthene di-hydrochloride. The amount of dipentene di-hydrochloride increases if the HCl be not quite dry or if an open vessel be used. Closed vessels and very dry HCl give the best results, and the reaction then succeeds even near 100° C., above which no solid product is produced. Pinene monohydrochloride compressed between folds of filter paper has a camphor-

like smell, but crystallized from alcohol or ether it has the form of beautiful white pinnate crystals, *but the camphor-like smell is retained by the alcohol, etc, and the purified crystals are inodorous.* It melts at about 125° C., and in so doing sublimes. According to Riban its melting-point in an atmosphere of HCl where it cannot dissociate is 131° C. It boils at about 207° to 208° C., undergoing partial decomposition. Its rotatory power is in the same direction as that of the pinene from which it is derived, − 30·6° (Wallach). In a closed vessel at 200° C., the acid is totally eliminated, Riban's terebene being formed. It is claimed that different reagents facilitate the separation of the HCl, viz. alcoholic potash, potassium acetate, sodium phenate, or stearate. This decomposition does not regenerate pinene, but one of its isomers, camphene. The conversion of pinene into camphene observed by Oppenheim was investigated by Berthelot. It also occurs when the hydrochloride is heated to 150° C. with aniline. Distilled over aqueous alkali and zinc dust solid pinene monohydrochloride is resolved into a highly volatile mobile *liquid* hydrocarbide.—[J. G. McIntosh.]

Preparation of Camphene from Pinene Hydrochloride, Hydration of the Product to Isoborneol, and Oxidation of the latter into Camphor. —Bertram employs camphene, prepared by freeing pinene hydrochloride from its acid constituent, and transforms it into isoborneol acetate by treating it with glacial acetic acid and sulphuric acid, isoborneol being obtained by saponification, and oxidized to camphor. The HCl in the pinene compound can be expelled by various means, such as heating with secondary bases, ammonia, alkali phenolates, alkaline solutions of higher fatty acids, or lead acetate dissolved in acetate acid. The camphene treated with aceto-sulphuric acid furnishes isoborneol, an oil boiling at 225° C. This, on saponification, deposits solid isoborneol, which is collected and purified by recrystallization from benzol or petroleum ether. The refined product is oxidized to camphor by means of potassium permanganate dissolved in water or acetone, by gaseous chlorine, ozone, nitrous acid, air, and oxygen, nitric acid containing nitrous acid, or by hypochlorites.

Action of Acids other than HCl *on Oil of Turpentine.*—According to the patent specification of the Ampère Electrochemical Co., camphor is obtained direct with bornéol and isoborneol esters by the action of anhydrous oxalic acid on oil of turpentine. This is, however, inaccurate, but the borneols obtained by saponifying the esters can be converted into camphor by oxidation. The yield is too small to be profitable. The works like many others had to be closed down after a large sum of money had been sunk in the venture, and the patent was allowed to lapse. Similar processes were introduced by Von Heyden and O. Schmidt, the former using salicylic and analogous acids, the latter chlorobenzoic acid; but the yield in both cases was too small to be profitable.

Action of Acetates on Pinene Hydrochloride.—This reaction

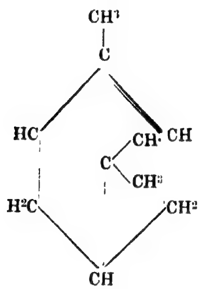
furnishes isoborneol acetate, which is then saponified by alkali and oxidized into camphor. Lead acetate, or preferably zinc acetate, dissolved in glacial acetic acid is used, but no definite information is available as to the practicability of the method.

Action of Magnesium on Pinene Hydrochloride.—In the Hesse process the Grignard reaction is used, the resulting complex compound of pinene hydrochloride, magnesium, and ether being oxidized with air and converted into magnesium chloride and borneol by treatment with dilute acids. The borneol is oxidized into camphor in the usual manner. The unreliability of this complex reaction and the high price of magnesium militate against the success of the method.

Camphene, a solid terpene, occurs in three isomeric forms. First observed by Opperman, it was isolated and defined by Berthelot, who prepared the lævo, dextro, and inactive forms. If this terpene be widely diffused in essential oils, it has only been fully identified in few, as in *Pinus Sibirica*, whence Goluboff extracted a solid hydrocarbide $C_{10}H_{16}$, melting-point 30° C., boiling-point 162° C., which Bertram and Walbaum showed consisted essentially of camphene by converting it into isoborneol. They also found it in oil of citronella to the extent of 15 per cent, with dipentene $(C_5H_8)_2$; in essence of ginger, with phellandrene; in essence of kesso; in Japanese valerian; and in oil of camphor. By hydrating the fraction of American spirits of turpentine, boiling-point 160° to 161° C., they obtained some isoborneol; hence American turps contains a small amount of camphene. Bouchardat isolated a camphene from aspic oil, which, on hydration, gave isoborneol. Olivero found camphene in valerian oil. Essential oils which contain borneol generally contain camphene. Camphene may be prepared either from pinene or borneol. In the isomerization of pinene camphene occurs in the products from the action of concentrated sulphuric acid on pinene. Armstrong and Tilden prepare it by agitating spirits of turpentine with 1 per cent by volume of concentrated H_2SO_4. Pinene hydrochloride cedes its HCl to various reagents more or less readily, but pinene is not recovered; it is isomerized to camphene. But J. G. McIntosh has shown that distillation over reducing agents like zinc dust yields a *liquid* hydrocarbide. Riban prepared inactive camphene by heating pinene hydrochloride for twenty-four hours at 180° C. (356° F.). In exactly the same way but using sodium stearate he obtained lævo-camphene $[\alpha_D]$ − 63°. But alcoholic potash acting for seventy-two hours at 180° C. (356° F.) yielded a less active camphene $[\alpha_D]$ − 57°. But these were only mixtures, rich in camphene or in mixtures of active and inactive camphene. Bouchardat and Lafont found a higher rotatory power than Riban, 80°. Prolonged contact with the reagents modifies the rotation. Wallach uses sodium acetate in acetic acid and heats for three to four hours at (about) 200° C. (392° F.) but not beyond. The camphene is separated from the undecomposed pinene hydrochloride by steam distillation (?). Reychler

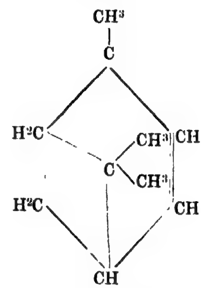
heats in open vessels with carbolic acid. He mixes the hot carbolic acid with the potash, or soda, required to eliminate the chlorine, heats for a few minutes to 170° C. to expel all water, and then adds the pinene hydrochloride without allowing the temperature to fall too low. He then heats with an ascending condenser, keeping the temperature at 155° to 165° C. for thirty minutes. The mixture is then distilled until the thermometer marks 185° to 190° C. After washing with potash an almost pure camphene is obtained, boiling-point 153° to 163° C. The yield is about 75 per cent of theory.

$C^{10}H^{16}$



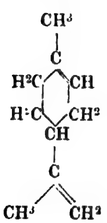
Pinene.

$C^{10}H^{16}$



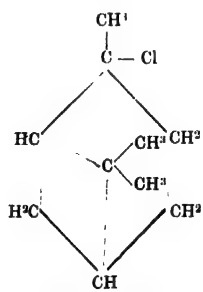
Camphene.

$C^{10}H^{16}$



Dipentene.

$C^{10}H^{16}$



Artificial Camphor.

Laurel Camphor, $C_{10}H_{16}$. *Origin.*—To the concrete volatile oil existing abundantly in almost all parts of plants of the laurel tribe, but especially in the camphor laurel, *Laurus camphora*, the Arabs, who introduced it into Europe in the fifth century, gave the name of *kaphur*, hence camphor. In India the vernacular names are very similar to each other. Just as we have camphor (English), camphre (French), camfora (Italian), the Sanskrit is karpura, Arabian, kaphur, and Hindustani, kaphur. These designations are probably derived from the Javanese kapur, which seems to indicate both lime and camphor.

The term camphor, originally a specific name, was soon corrupted in Europe to a generic one so as to be used indiscriminately (in the same fashion as "resin" now is, both of which terms, if comprehensive, are equally vague and equally misleading) to designate quite a series of volatile, solid, natural, crystalline products possessing a characteristic odour and special physical properties (peppermint, anise, bergamotte, patchouli camphors). The term, however, is now restricted to the substance under consideration, viz. that existing in the wood of the camphor laurel and several other trees of the family of *Laurinaceæ*, growing particularly in Japan, Sumatra, Java, and Borneo, in the essences of rosemary, sage, sassafras, marjolaine, and the Reunion basilic. The camphor laurel is a fine, evergreen tree, and, except in size, bears some likeness to the common laurel of our shrubberies. It reaches a height of 50 feet with a girth of 20 feet. The leaves are small, elliptical, lustrous, vivid green, and the berries are like black currants. The trunk usually grows to the height of 20 feet, and then spreads out into branches. The trees live to a great age, over 100 years, trees of this age being those that are selected to be felled for the extraction of camphor, as at that age they are richest in that product. Some trees attain a diameter of 20 feet. There are fine trees in the Botanic Gardens of Calcutta and Sahranpur; it thrives in Dehra Dun and in the Nilghiris up to altitudes of 7000 feet.

Formosan Extraction Process.—The extraction process is crude in the extreme, being carried out by peasants who only make a precarious living at the work. The trunk, branches, roots, etc., of the felled tree are broken into chips. The chips are run into a wooden tub which stands on and fits closely to the top of an iron pan filled with water which is kept boiling by a fire underneath. The bottom of the tub is perforated so that the steam may pass through the chips. A steam-tight cover is fitted to the top of the tub. The steam rising from the water in the pan passes through the tub, and in its passage extracts the camphor and the camphor oil from the chips and carries them in a state of vapour through a bamboo pipe fixed to the tight-fitting lid of the tub. This trough is divided by vertical partitions into compartments, communicating with each other, at alternate ends, so that the vapours travel successively through each compartment in the trough from one end to the other. All the camphor and camphor oil are condensed in these compartments, together with a portion of the steam. The uncondensed steam escapes into the air through a pipe fitted to the condenser. A continual stream of water flows from a wooden pipe into a wooden trough placed over the condenser. From this upper trough the water flows into the third or lowest one, thus keeping the condenser cool during the whole course of the distillation, which lasts about twenty hours.

Fresh water is then run in through the top of the tub into the

pan for the next distillation, and being thus heated in its passage through the hot chips, time and fuel are saved in the next heating of the pan. The tub containing the chips is emptied and the latter, after drying, are used as fuel. The tub is then re-charged, well closed, and the distillation proceeded with as before. As the distillation proceeds a semi-solid distillate of camphor and camphor oil collects in the compartments of the trough, floating on the water in the condensed state. This is allowed to accumulate until several charges have been distilled, being usually removed at intervals of from five to ten days. The relative proportions of solid camphor to liquid camphor oil varies with the temperature of the surrounding atmosphere. In summer only 2 per cent per diem of solid camphor is obtained from the wood, whilst 3 per cent is obtained in winter. In summer 18·04 litres of liquid oil are obtained from the semi-solid distillate produced during a ten days' distillation, whilst only 5 to 7 litres are obtained in winter. Formerly the crude oil containing a large per cent of camphor was considered useless, but it is now re-distilled from iron stills connected with a brass worm condenser.

The distillate is collected in suitable vessels, cooled and filtered or pressed to separate the solid camphor, and the filtrate still containing camphor is mixed with a fresh quantity of oil and again distilled and the distillate cooled and pressed as before. Working in this way 20 to 25 per cent of solid camphor is obtained from the quantity of crude oil distilled, the latter losing half of its bulk during the process.

Ceylon Process of Camphor Extraction.—In a recent communication from the Government of Madras an extract from a lecture delivered before the Ceylon Agricultural Society, by Mr. M. K. Bamber, is given in full. The extract is as follows: "The still required for the purpose is of the simplest description and very similar to that used by the Japanese in Formosa, with slight improvements in the condensers, as perfect condensation is absolutely essential for success. The slightest smell of escaping camphor may mean a loss of 20 per cent or more, as has been proved by several experiments, and the two means of preventing it and obtaining the maximum proportion of camphor to oil are absolute condensation and slow distillation with a minimum of heat. The still may consist of an ordinary wooden cask, but is better if somewhat conical in shape, and should be about 6 feet high, 3 feet diameter at the bottom, and 2 feet 6 inches at the top, and have a close-fitting door at the lower end for the removal of the refuse prunings. The top, or a portion of it, must be removable but capable of being hermetically closed. From near the top a large diameter bamboo, 5 feet to 7 feet long, passes to the condensing boxes of wood placed in a suitable tank, and connected with short lengths of similar bamboo. The still has a perforated bottom and stands over an iron basin built into a small stone or

brick furnace. The basin, about 2 feet 6 inches to 3 feet in diameter, is fitted with a supply tube for adding water as required, and an overflow pipe closed with a plug during distillations. The condensing boxes consist of bottomless boxes of suitable size, having three or more partitions in each, with communications at opposite ends of each division to ensure thorough circulation of the camphor and water vapours. The tops of the boxes are hermetically closed about 1 inch below the upper edges, and the boxes are stood in the tank as mentioned above, being connected by short bamboo lengths. Cold water from a stream flows from a pipe or bamboo on the top of each box and then overflows into the tank, which has an outlet pipe 2 inches to 3 inches from the bottom. By this means a water seal 3 inches deep is kept round the bottom of the boxes. The mixture of camphor vapour and steam from the still enters the first box just above the water level, circulates round the various partitions, and so passes from box to box, the camphor being condensed in pure white crystals on the walls and partitions as it cools down. The last box is fitted with an outlet of bamboo, which can be kept closely plugged with straw. This acts as a safety valve, and enables one to ascertain whether condensation is perfect, as there should be little or no smell of camphor observable. In working, the still is loosely filled with the fresh prunings as brought in, the top put on and well luted with clay, water poured into the basin, and a fire lit to bring it rapidly to the boil. As soon as this occurs and a slight smell of camphor or eucalyptus can be smelt at the escape tube on the last box, the fire is reduced and the water merely kept hot for several hours. A good plan is to have a glass let into the cover of the first (or all) of the condensing boxes, and as soon as vapour begins to condense on it to immediately reduce the fire to a minimum, as the object to be gained is to drive off all the camphor with as little steam as possible. A small wooden spigot in the top of the still makes it possible to ascertain when all smell of camphor has disappeared, but care must be taken when opening it not to become scalded. When completed, probably in three to four hours, the door at the bottom of the still is opened, the prunings removed and the still re-charged from the top. All water in the pan, which contains much tannin, etc., in solution, is changed by opening the overflow plug, and pouring in a fresh quantity through the supply tube. During distillation it is necessary to occasionally add some water to the pan to maintain a constant level and prevent burning. To save time it would be best to have two stills connected with the condensers as with many citronella grass stills, since the one could be filled while in the other distillation was proceeding; the latter could then be allowed to cool down before opening without a loss of time. To preserve the heat in the top of the still and ensure the camphor passing away readily, the still should be thickly coated with clay or other non-conducting material, the Japanese method

being to surround the still with cane-work and ram clay into the space between. When a condenser is seen to contain sufficient camphor, it should be opened and the camphor carefully scraped out, every precaution being taken to keep it free from dirt or fragments of any description ; otherwise re-distillation would be necessary if the best price is to be obtained. A wooden scraper should be used, contact with metal being avoided as far as possible while in the moist condition. The camphor should be placed in a well-made box like a tea-chest, having a perforated false bottom 4 inches or 5 inches from the actual bottom, and the top perfectly closed. In a few days most of the oil will have drained into the lower portion of the box, which should be zinc-lined, and the dry camphor can be removed and carefully packed in zinc-lined cases for dispatch. By reducing the camphor oil to a low temperature fully 50 to 60 per cent of solid camphor separates out and can be removed with a cloth strainer and well drained, the temperature being kept as low as possible while the excess of oil is draining away. Should any of the camphor be accidentally discoloured, it should be thrown back into the still, with a subsequent charge of prunings for re-distillation. The chief uses of camphor are for the manufacture of celluloid, smokeless explosives, fireworks, etc., and medicinally in the treatment of influenza, dysentery, and cholera. For the latter disease it was used most successfully in Naples in 1854, all the cases treated recovering, and it was employed with equal success in Liverpool in 1866. Any outbreak of influenza increases consumption at once, but the chief demand is for the manufacture of smokeless powders and celluloid ; it is also said to be employed in one of the numerous rubber substitutes now manufactured."

Extraction of Camphor from Leaves and Young Branches.—The ever-increasing consumption of camphor induced Hooper, the Indian Government Quinologist, etc., at Ootamacund on the Nilghiri Hills, to ascertain whether the leaves and young branches, hitherto wasted, could not be utilized as sources of camphor. Leaves from the Botanic Garden at Ootamacund yielded on this distillation 1 per cent of essential oil of density 0·9322 at 15° C., deviating + 9·4 in a 200 mm. tube and containing 10 to 15 per cent of camphor. Leaves from Nadavatum on the Nilghiris yielded a product with 75 per cent of camphor, the density of the expressed oil = 0·9344 at 15° C. It deviates + 54°, d = 200 mm. The difference in the percentage was due to the different altitudes, Ootamacund being 7300 feet and Nadavatum only 1000 feet.

Camphor Cultivation in the Malay States.—Experiments have been made with the propagation of camphor by means of cuttings. The first trial of some thousands of these was not successful owing to lack of supervision, but more have been struck, and it is hoped to be able to produce a stock of young plants. While not recommending that the cultivation of camphor should be taken up over large areas, the report of the Director of Agriculture points out

that the price of camphor is exceedingly high, and the prospects of high profits are excellent. The growth of the trees at the experiment station is most encouraging, and compares very favourably with trees of the same age in Ceylon, even at higher elevations, which are supposed to be more suitable for camphor cultivation. Some 300 trees at the Experimental Plantations at Batu Tiga, growing only a few feet above sea-level, have in two years attained a height of from 12 to 14 feet.

The camphor trees of Formosa are mostly trees which are old and do not produce seeds, and even when such as do produce seeds are found, they are so remote in the savage districts that it has been found impossible to make use of them. Consequently the seeds which have been used for plantation have mostly been brought from Kiushiu and Shikoku, in Japan. The time for sowing is in the spring and autumn. The Government has shown great energy in establishing plantations, the first being made in 1896. When the camphor monopoly was established in 1899, fresh plantations were made, and in addition to the main plantation there are now two plantations in Taihok'u prefecture, four in Taichu, one in Tainan, and one in the district of Gilan. The cultivation of camphor trees has lately been attended with very successful results, the number of young trees suitable for transplantation reaching more than 1,000,000. The camphor refinery at Taihoku is capable of turning out 1800 lb. of refined camphor and 5800 catties of Class A camphor per day. There are 4 officials in charge of the refinery, assisted by 32 Japanese operatives, of whom 14 are male and 9 female, and 45 Chinese operatives, of whom 36 are male and 9 female. Most of the machinery used was made in Japan. There is a branch office of the camphor bureau at Kobo, to which a refinery is also attached. There are 3 officials in charge, with 38 male operatives and 21 females. This factory is capable of turning out 1000 lb. of refined camphor and 2000 catties of Class A camphor per day.

Camphor occurs in three (purely physical) isomeric forms only differentiated by certain optical and thermic properties. The calorific intensity of dextro- (ordinary laurel) camphor is 1402·2 calories, of lævo-camphor 1414 calories, and racemic camphor 1413·4 calories. Lævo-camphor occurs in essence of matricari parthenium. Inactive camphor occurs naturally and may be prepared synthetically by mixing two active camphors. The molecular rotatory power of pure camphor is, according to Haller,

$$[\alpha]_D = \pm 42^\circ \text{ and } [\alpha]_D = \pm 43^\circ$$

in alcoholic solutions containing 1 molecule per litre. Camphors of molecular rotatory power lower than 42° occur in natural essential oils. These are mixtures of lævo- and dextro-camphors. So also are the camphors got by oxidizing natural mixtures of lævo- and dextro-borneols. Bouchardat and Lafont in oxidizing the

borneols from the action of acetic acid on French spirits of turpentine got camphors of abnormal rotations, $-67{\cdot}2^\circ$, $-71{\cdot}4^\circ$, $-51{\cdot}1^\circ$, and $-53{\cdot}5^\circ$, evidently isomers of the natural product. Jungfleisch, Tilden, and Armstrong describe real inactive camphors, but their real inactive nature as distinguished from compensation is not satisfactorily demonstrated. The rotatory power of dissolved camphor varies with the concentration ; it increases therewith in varying proportion according to the solvent. Forster gives the following formula for benzol solutions :—

$$[\alpha]\frac{20}{\mathrm{D}} = 39{\cdot}755 + 0{\cdot}17254\ \mathrm{C}.$$

in which C = concentration (grammes of camphor) in 100 c.c. of liquid. With alcoholic solutions the formula is :—

$$[\alpha]\frac{20}{\mathrm{D}} = 41{\cdot}982 + 0{\cdot}11824\ \mathrm{C}.$$

The rotatory power of camphor dissolved in vegetable oils is, contrary to what occurs with benzene and alcohol, perceptibly proportional to the strength.

Physical Constants.—Melting-point of pure camphor, 177° to 178° C. ; boiling-point, 205·3° C. (Kuhara) ; 209·1 under a pressure of 759 mm. (Forster) ; specific gravity at 200° C. = 0·891. Its molecular refraction for the ray D is 74·43 (Krannonikoff) and 74·32° (Gladstone). These figures correspond with a saturated compound. Camphor may be detected in admixture by its boiling-point (205° to 210° C.), its smell, its crystals, and the boiling-point of its oxime. Borneol, if also present, must first be extracted by the phthalic ether or succinic acid methods without the use of sodium, but in sealed tubes. To isolate camphor from pharmaceutical products caustic soda lye is added and the camphor distilled over in an atmosphere of steam. Forster estimates camphor directly by collecting the entrained product in benzene, examining the benzene solution at 20° C., and applying the formula :—

$$2{\cdot}51536\frac{a}{y} - 0{\cdot}02746\left(\frac{a}{y}\right)2,$$

in which a is the deviation observed, y the length of the tube in decimetres.

TABLE LII.—ROTATORY POWER OF LAUREL CAMPHOR.

Solvent	°C.	Limits of Concentration.	Sign.	Rotatory Power $[\alpha]_D$
Alcohol ethylic .	20	$q = 45\text{-}90$	+	$54{\cdot}38 - 0{\cdot}1614\,q + 0{\cdot}000869\,q^2$
" methylic	20	$q = 50\text{-}80$	+	$56{\cdot}15 - 0{\cdot}1769\,q + 0{\cdot}000610\,q^2$
Acetic acid .	20	$q = 34\text{-}84$	+	$55{\cdot}49 - 0{\cdot}1372\,q$
Ethyl acetate .	20	$q = 46\text{-}85$	+	$55{\cdot}15 - 0{\cdot}04383\,q$
Benzene . .	20	$q = 36\text{-}76$	+	$55{\cdot}21 - 0{\cdot}0168\,q$

Properties.—Camphor is easily distinguished from other substances by its whiteness and ice-like semi-transparency, by its warm, aromatic taste, and its sharp, penetrating, rosemary-like odour, which persistently adheres to the hands and spreads widely through the surrounding atmosphere. It has the density of 1 at 0° and ·992 at 10° C. Its vapour tension at the ordinary temperature is sufficient to cause it to sublime in hexagonal plates on the sides of the stoppered bottles in which it is kept. It melts at 175° C. and boils at 204° C. without decomposition. It has, in fact, so great a tendency to volatilize that it gradually evaporates into the air when exposed and disappears altogether, leaving not a single trace of its existence. It is very combustible, and suddenly bursts into flame when brought in contact with a lighted taper, and burns with a white, brilliant, very smoky flame, acrid and strong smelling. It even burns when placed on water on which it floats. *Gyratory Motion.*—Water only dissolves $\frac{1}{1000}$ part of its weight, nevertheless it acquires its taste and smell. A fragment of camphor thrown upon water assumes a gyratory motion, which stops as soon as a drop of oil is thrown on the surface of the liquid. A cylinder of camphor of 4 to 5 mm. in diameter, one part of which dips into the water whilst the other part remains in the air, communicates a to and fro movement to the water, and after the lapse of a few days is cut a little above the line of flotation. This remarkable occurrence is due to the simultaneous evaporation of the camphor and the water, which is most active at the surface of the liquid. *Solvents.*—Alcohol is the best solvent for camphor; 100 parts of this vehicle dissolve 120 parts of camphor in the cold. It is precipitated from its alcoholic solution by water in finely divided flakes. This is the best method of obtaining it in a fine state of division, because owing to its elastic nature it is very difficult to grind in the ordinary way with a pestle and mortar, at least without having been sprinkled with alcohol. Dissolved in weak spirits of wine it forms camphorated brandy, which is so often employed as an embrocation to disperse coagulated blood due to cuts or blows.

It dissolves freely in ether, fatty oils, acetic acid, etc. When it is desired to suspend it in water in a divided state, it is triturated with egg yoke. Its solution in nitric acid was formerly erroneously known as oil of camphor.

Camphoric Acid, $C_{10}H_{16}O_4$.—If camphor be distilled with eight times its weight of nitric acid it is converted by the oxygen of the latter into a white, slightly bitter acid, which crystallizes in feather-shaped crystals, freely soluble in water. This acid, discovered in 1785 by Rosegarten, is known as camphoric acid, melting-point 62·5° C. Treated with sulphurous acid gas, camphor yields the liquid disinfectant known as *thiocamf*. During the process the camphor liquefies and absorbs a large quantity of sulphurous acid. By spontaneous evaporation this solution gives off the combined vapour of sulphurous acid and camphor.

Adulterations.—Pinene monohydrochloride, detected by lower boiling-point and evolution of hydrochloric acid fumes on heating.

Uses.—Camphor is used as an ingredient of fireworks, not only on account of its great inflammability but also because of the whiteness of its flame. Its smell is supposed to be fatal to small animals, especially insects. This explains the use of camphor in cases containing natural history specimens. It prevents moths and other insects from laying their eggs thereon. For the same reason small satchels containing camphor are placed in drawers in which hats, fur, and woollen articles of dress are stowed away. Camphor is added to varnishes to increase their lustre, elasticity, and to facilitate the solution of refractory resins in the manufacture of spirit varnishes. But the lustre induced by camphor is not very permanent. Terpineol is now more in vogue as an aid to solution.

Borneo Camphor, Borneol, Camphol, $C_{10}H_{18}O$, first described by Pelouze, is obtained from the *Drybalonops aromatica* (*A. gaertn*), a lofty *Dipterocarpus* tree native in the North-west Coast of Dutch Sumatra, North Borneo, and Labuan. Coarse crystals of borneol are formed in the stem. These constitute the Barus camphor, called in Indian returns Chimsaini or baris. The crystals are often found in concrete masses in the heart of the tree, or in the knots and swellings where the branches issue, but camphor is also found beneath the bark. To obtain the product, which is valued by some of the Chinese at from 40 to 80 per cent, and even a hundred times the price of ordinary camphor, the tree is destroyed and cut up into small cross pieces which are then split up with axes to expose the ordinary camphor. An average tree is said to yield about 11 lb., but 22 lb. are sometimes extracted from a single tree. The old trees are the most remunerative, and only about 10 per cent of those destroyed will repay the labour. This camphor is used by the Chinese for embalming and ritualistic purposes, and is well paid for. "Probably," says Watt, "the camphor first known to the world was obtained from this tree and not from *Cinnamomum*" (*Laurus camphora*). Borneol is also met with in small quantities in essence of valerian, where it is formed, according to Gerhardt, by the hydration of bornene previously present therein. *Preparation of Borneol.*—By heating ordinary camphor from eight to ten hours with an alcoholic solution of potash from 180° to 200° C., Berthelot resolved laurel camphor into camphate of potash and borneol. Baubigny used sodium thus:—

$$\underset{\text{Camphor.}}{2C_{10}H_{16}O} + 2Na = \underset{\text{Sodic Camphate.}}{C_{10}H_{15}NaO} + \underset{\text{Sodic Borneolate.}}{C_{10}H_{17}NaO}.$$

The borneol so obtained exhibits all the properties of natural borneol. Its rotatory power is, however, greater. Borneol is also formed in small quantity when amber is distilled with dilute caustic potash. It differs from natural borneol by its more feeble rotatory power.

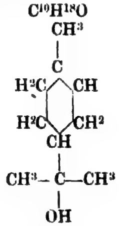
Properties.—Borneol is found as small, colourless, transparent, friable crystals; its smell recalls both ordinary camphor and peppermint; its taste is ardent; it melts at 198° and boils at 212° C. (about 220° C. according to Berthelot). It deviates the plane of polarization to the right. It is insoluble in water, but is very soluble in alcohol and ether.

Reaction.—Hot nitric acid converts it into ordinary camphor:—

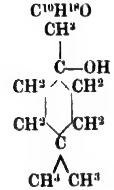
$$C_{10}H_{18}O_2 + O = C_{10}H_{16}O + H_2O_2.$$

When borneol is distilled with anhydrous phosphoric acid, a hydrocarbide passes over isomeric with ordinary pinene, viz. bornene $C_{10}H_{16}$. When heated with concentrated hydrochloric acid, borneol is converted into a solid monohydrochloride isomeric with pinene monohydrochloride. Berthelot has described combinations of borneol with stearic and butyric acids. Borneol is an alcohol or pseudo-monatomic alcohol. There exists in the oil of garance a residue obtained by the distillation of garance alcohol, a borneol identical in its chemical properties with borneo camphor, but which deviates the plane of polarization to the left. The essential oils of cajeput and coriander contain an oxidized principle isomeric with borneo camphor.

$C^{10}H^{18}O$



$C^{10}H^{18}O$



Terpineol.—Melting-point, 35° C.; distils at 218° C.; exists as acetic ester (terpineol acetate in essence of cajeput). It is obtained either by dehydrating terpin or by the dehydration of spirits of turpentine by sulphuric acid. Terpineol has a pleasant odour of lilac. It is inactive, but an active terpineol is known, obtained by aid of dextro-limonene, which boils at 215° C.; oxyoxime melts at 134° C.; yields terpenylic acid by oxidation. Becomes rather prominent as a solvent for copal without previous fusion, thus taking the place of the camphor of old, also as a solvent for rubber.

Terpineol (isomer).—Boiling-point, 69° to 70° C., with the same lilac odour.

Camphor Oil.—The crude oil after repeated distillation yields refined camphor oil, a colourless liquid which like solid camphor burns with a bright smoky flame. It has a specific gravity of 0·95, that of the crude oil being 0·959. It is oxidized into ordinary camphor by the action of air, oxygen, or nitric acid. It is a good solvent for various resins, such as mastic, elemi, gamboge, dragon's blood, rosin, asphaltum, sulphur.

Camphor Oil Varnishes.—When 8 lb. of mastic or such-like resin is dissolved in 10 lb. of camphor oil and the solution thinned with 3·3 lb. of spirits of turpentine, a transparent paper varnish is obtained which dries with a bright gloss.

An elastic waterproof varnish is obtained by dissolving linoleate of magnesia or other insoluble linseed oil soap in camphor oil with the addition of a solution of a resin dissolved in the same solvent.

But these varnishes soon lose their lustre, which is in large measure due to the camphor dissolved in the camphor oil. Consequently, however brilliant they may be at first, they become dull as the camphor, etc., evaporates.

Black camphor oil is used in antifouling compositions. The comparative solvent action of camphor oil on varnish resins is shown in the following table :—

TABLE LIII.—COMPARATIVE TABLE OF THE SOLUBILITY OF RESINS IN LIGHT AND HEAVY CAMPHOR OILS AND OTHER ESSENTIAL OILS.

100 parts by weight of the undernoted Essential Oils Dissolve—	The following Resins in the undernoted proportions:—						
	Amber.	Rosin.	Copal.	Dammar.	Mastic.	Shellac.	Yellow Wax.
Cajeput . . .	6·53	43·70	5·52	42·49	41·16	0·66	—
Copaiba . . .	—	24·95	0·00	34·57	—	—	4·49
Light camphor oil .	9·73	46·16	9·16	34·95	35·04	1·33	—
Heavy " " .	6·50	31·35	2·81	50·08	37·98	0·83	—
Lavender . . .	—	52·86	—	33·07	—	—	9·34
Cloves . . .	—	79·79	0·00	18·27	—	—	—
Rosemary . . .	10·16	48·94	4·81	99·44	21·39	0·79	—
Alspice . . .	8·90	40·98	9·51	41·66	33·47	3·67	—
Turpentine . .	7·47	51·84	—	64·28	52·79	12·94	—
" rectified .	10·30	—	6·47	—	—	—	8·10
Paraffin oil . .	—	—	—	9·27	—	—	4·16
Wax oil . . .	2·87	—	—	67·31	—	—	5·64

TABLE LIV.—FRACTIONAL DISTILLATION OF LIGHT CAMPHOR OIL.

°C.	Vol.	°C.	Vol.	°C.	Vol.	°C.	Vol.
35-150	12	164-166	6·0	174-176	21·8	184-186	3·0
150-155	5·5	166-168	6·9	176-178	12·7	186-188	4·0
155-160	3·6	168-170	10·0	178-180	12·7	188-190	3·6
160-162	9·0	170-172	13·6	180-182	9·0	190-198	4·5
162-164	7·3	172-174	14·5	182-184	11·8	Residue [1]	25·0

[1] Total distillate and residue up to 198° C. 188·5 c.c., loss 1·5 c.c.

TABLE LV.—FRACTIONAL DISTILLATION OF HEAVY CAMPHOR OIL.

°C.	Boiling-point.	Percentage.	Formula.	°C.	Boiling-point.	Percentage.	Formula.
145-155	150	0·4	$C_{10}H_{16}$	202-206	204	10	$C_{10}H_{18}$
158-161	159	12·0	,,	212-214	213	30	$C_{10}H_{16}O_2$
167-169	168	13·0	,,	230-235	23[illegible]	7	$C_{10}H_{18}O_2$
170-171	171	5·0	,,	245-248	247	2	—
175-177	176	15·0	$C_{10}H_{18}O$	250-280	—	19·6	—
180-182	180	4·0	$C_{10}H_{16}$	—	—	—	—

Light Camphor Oil serves to mask the bad smell of common soaps. It was used to clean lithograph blocks, but now it is too dear. It is used in varnish-making for the same purposes as spirits of turpentine.

Heavy Camphor Oil is a greenish-brown liquid, the density of which has come down from 1·1 to 0·960. Its quality has degraded in the same ratio. It now only contains traces of safrol. It is soluble in all proportions in alcohol. Camphor oil was examined by H. Yoshida, who found pinene (7 per cent), a hydrocarbide distilling at 172° to 173° C., somewhat analogous to limonene (20 per cent), camphor (22·8 per cent), and camphor-eugenol, distilling at 212° to 213° C. (50 per cent), which, when kept boiling for some time, partly polymerizes with production of camphor. Acetic and benzoic anhydride convert camphor-eugenol into ethereal derivatives with formation of a small quantity of camphor. Sodium and alcohol change it into borneol, zinc chloride into cymene. In this reaction it is probable that camphor is formed as an intermediate product. But Schimmel's chemist could not find camphor-eugenol, and states that the product boiling above 212° contains ordinary camphor, safrol, and an unknown body boiling at 230° C., as well as small quantities of eugenol. The same authorities got on distilling different organs of the Yokohama *Laurus camphora* 1·8 per cent of an essential oil from the leaves which solidified at the ordinary temperature; from the roots 4 per cent of an essential oil, of density 0·957 at 15° C., containing much camphor, of melting-point 175° C. The liquid portion boils between 165° C. and 270° C. and has all the properties of commercial camphor oil.

N.B.—Since the above chapter has been in print, a U.S.A. Consul reports that the *Blumea balsamifera*, which yields a camphor identical with Borneo camphor, is being successfully exploited in Burmah.

CHAPTER XIII.

WOOD TURPENTINE—WOOD TAR—WOOD CREOSOTE.

The Preparation of Tar and Turpentine in Russia.—The material used for the production of tar and turpentine in Russia is tree stumps and waste timber, charcoal being also obtained as a by-product. Great advances have been made in the manufacturing process since the introduction of tar ovens made of steel plate, as these enable the tar oils and pyroligneous acid to be recovered, instead of being wasted as they were under the old system of charring the wood in heaps. At the same time the operation can now be carried on all the year round, and is not restricted to the summer, as was formerly the case. A usual way of working these ovens is in pairs, with a single still common to both, this method giving the best results with the smallest expenditure of labour. Since the success of the operation greatly depends on the uniformity with which the oven is heated, this has to be constantly controlled by means of a thermometer, mounted on the oven in such a manner as to record the expansion or contraction of the metal plates by a pointer moving over the surface of a number dial. In this way all fluctuations of temperature are rendered visible to the man in charge of the oven. Each oven is charged with about 8400 cubic feet of tree stumps, weighing 12,000 lb., the oven door being bricked up, the lid put on, luted with clay, and covered with a layer of about 6 in. of sand. The fire is then started, and at the end of about seventeen and a half hours the first runnings of spirit begin to come over. The operation is complete in 105 hours, and the maximum temperature does not exceed 26° C. The several distillation products, turpentine, tar, and wood vinegar, escape continuously from the various spouts of the distilling apparatus into the receptacles placed to catch them. When ten hours have elapsed after the heating has terminated, the oven is opened and the products weighed. The yield is approximately as follows: Turpentine spirit, 450 lb.; tar, 1300 lb.; charcoal, 2560 lb.; pyroligneous acid, 3700 lb.; tar oil, 28 lb.

Russian White Pine Oil.—In about a year, says a correspondent, a new rural industry has developed in the Vyatsk department, namely, the production of so-called white-pine oil. Within the limits of the Yakschinsk, Vozhgalsk, Phillipovsk, Sulaievsk, and Selesnevsk districts a hundred peasants' factories have already been erected for the distillation of this product. The foundation of the

industry was laid by a peasant of the Yakschinsk district. The simplicity of the plant and the cheapness of it, and the good profit in the business resulting from the cheapness of the raw material and the good prices obtained for the finished product, induced many to follow his example. The cost of a plant is about £10; but the carrying out of the process calls for some skill. The profit is three roubles (6s.) in twenty-four hours. From a pood of young pine wood about ½ lb. of oil is usually obtained in one of these plants, that is to say, 80 poods of wood are required for about one pood (36 lb.) of oil. A load of 20 poods costs 40 to 60 copecks (10d. to 1s. 3d.), so that on the average the cost of the raw material is about 2 roubles (4s.), and the price got for the oil is 5½ roubles (11s.) to 6 roubles (12s.) per pood (36 lb.). The sale of the product is completely assured in the town of Vyatka, which is visited by many buyers. Everything points to a further successful development of the business. [The reports as to the Russian turpentine industry are very conflicting. Others are as pessimistic as this is hopeful.]

American Retort Tar versus *Kiln Tar*.—Retort tar from pine knots and stumps is marketed about one dollar and a half under the price of kiln-burnt tar. To give this new product a fair test, several large rope manufacturers made purchases of sizable lots, but found that it was not suitable for their purposes. It is claimed that the new product lacks several important properties, which are lost through the new process of distillation. One important ingredient which is eliminated is *the oil in the tar*, which goes over in the course of distillation. Cordage men claim that when the retort tar is applied the rope, instead of showing a straw colour, shows a dirty chocolate colour, which has met with decided disfavour in the trade, and difficulty has been experienced by rope manufacturers to market their product, and in many instances losses have been incurred on goods turned out with the retort tar. Oakum and dry-dock firms do not favour the tar, because of the lack of oil. It remains to be seen whether these objectionable points can be remedied in order to make it satisfactory to the rope manufacturers, who are the heavier consumers of wood tar. The retort tar, however, is being used for various other purposes, but up to now has not filled the expectations of the consumer. There will, doubtless, be found use for all the retort tar produced, as it is sold at a lower price, and therefore available where the high cost of kiln tar makes its use impracticable. It may be that the objectionable features can be overcome by change in method of production, and the product be made in every respect equal to the other.

Retort Tar Oils, Retort Wood Tar.—The crude tar produced when wood is distilled in retorts varies from 3 to 10 per cent of the wood. The portion separated from the crude pyroligneous acid by settling and that skimmed from the top of the neutralized acid are mixed, and, after washing with water, are sold in the crude state as "raw tar" or as "retort tar". It is used for preserving wood, for

roofing-felts, as an antiseptic, for making wagon grease and other low-grade lubricants. It is also a suitable raw material for the preparation of aniline colours, but finds no application as such, because of the low price of coal-tar, and because the composition of the latter is better understood. Besides the tar separated by settling, the crude pyroligneous acid contains considerable tar held in solution by the acids and alcohol present, which is recovered when the crude acid is distilled, and constitutes what is known as "boiled tar". It may be sold as such or burned under the retort, or it may be mixed with the raw tar and subjected to any desired treatment. Wood tar, which varies in character with the kind of wood from which it is obtained, is a thick, dark-coloured, viscous material still containing some acetic and other acids, and has a specific gravity of about 1·05 to 1·15. It consists when derived from hardwood chiefly of paraffins, toluene, xylene, cresol, guaiacol, phenol, and methyl derivatives of pyrogallol. The tars derived from coniferous woods constitute the chief tars of commerce, and are particularly rich in terpenes, contain considerable quantities of rosin, and have a much greater commercial value than those derived from hardwoods. By far the greater part of the tar derived from hardwood distillation is burned under the retorts.

Wood Turpentine.—This product, when properly made and refined, has a specific gravity of from 0·860 to 0·880 at 20° C., though the first runnings from the still may have a lower and the last runnings a higher specific gravity; 95 per cent should distil between 150° and 185° C. This turpentine closely resembles spirits of turpentine from the oleo-resin of tapped pines, and sells for from two to ten cents less per gallon (depending on the care with which it has been refined) than the latter, for which it has been used as a substitute and adulterant. The processes of production and the technical value of this material are now being studied by the technical experts of the U.S.A. Forestry Department, but as the work is not completed, no conclusion as to the relative value of wood turpentine as compared with ordinary spirits can be given. A few words may be of interest, however, as to the best methods of producing, refining, and marketing this article. When wood turpentine was first placed upon the market it was very irregular in composition, owing to the fact that but little was known of its nature, and producers were unacquainted with the proper methods of refining. As has been stated, turpentine as commercially produced is not a definite compound, but a mixture of closely related terpenes, and consequently it differs from moment to moment while distillation is taking place, and its distilling temperature rises, so that the turpentine obtained at the close of a dry distillation is much heavier and differs in many ways, particularly in odour and colour, from the first runnings from the still. This statement applies as well to ordinary turps. The distiller seldom realizes the importance of this fact as affecting the uniformity of this product. In a few instances

the gravity of the distillate is taken as the turpentine passes from the condensers, and if the hydrometer is carefully watched and the specific gravity is not allowed to rise above 0·875, the resulting turpentine is fairly uniform and satisfactory. As a rule, however, the close of the turpentine distillation is determined by the appearance of the oil, the formation of beads or foam on the surface indicating that heavier oils are beginning to distil. As this point is usually not carefully watched, the result is that the product of a plant differs from day to day in colour, odour, and specific gravity, and its market value is lowered accordingly. Although considerable improvement has been made, wood turpentine still varies greatly in composition, much to its detriment commercially. That produced by steam distillation has, in well-refined turpentines containing but a small amount of heavy oils, a pleasant, fresh pine odour, and but little colour, while the heavier portions of the steam-distilled oils have a more penetrating and lasting odour, somewhat resembling that of camphor, and the more of these heavy oils the turpentine contains the stronger its odour, and the more it differs from gum turpentine in all its properties.

Turpentine produced by destructive distillation has a pungent, smoky odour, which the most careful refining will not entirely eliminate, and is usually more highly coloured than the steam-distilled product. The general character of the turpentine is determined largely, therefore, by the method of production, but it is further modified by the care with which it is refined. Every precaution should be taken to ensure that the temperature does not rise sufficiently high to drive over the heavy oils. If the refining still is heated directly with fire, a thermometer may be placed in the liquid and the heat so regulated that its temperature does not rise above 220° C.; or, if the still is properly constructed, the product may be controlled by taking the specific gravity of the distilled and cooled spirit.

Pine Stump Oil.—Bergstrom obtained a crude oil from *P. silvestris* stumps by superheated steam distillation at 180° C. Fractionated in a column still, this oil furnished about 50 per cent, boiling-point 156·5° C. (mainly d-pinene). Another large fraction, containing sylvestrene, came over at 171° to 178° C., and a third fraction, boiling-point 190° C., contained terpineols and oil of turpentine, apparently formed during distillation. Pure terpineols were got at 218° C., and these were transformed into acetate and back again into terpineols, which bodies impart the agreeable smell and sharp taste to pine-wood. Bergstrom obtained terpineol from the timber of *P. palustris*. The fraction distilling at 265° C. differs from the preceding by being levo-rotatory. It contains sesquiterpenes and cadinene. The still higher fractions contain sesquiterpene, alcohol, and have a bluish colour.

Rectifying Pine Oil.—The inferior oils of turpentine (pine oil) obtained by dry distillation are distinguished by a strong smell, which,

according to Hesse, can be eliminated by treating them with metals of the alkalis or alkaline earths, whereby the malodorous constituents are converted into a non-volatile form. The quantity of metal required is so small as to add but little to the cost of preparation of the oil, and, if necessary, the distillation from the metals in question may be preceded by a treatment with hydroxides of the metals of the same groups. The process differs from those in which the malodorous ingredients are oxidized, there being no destruction of the more valuable unsaturated components of the oil. As an example of the process, 1000 parts of Russian oil of turpentine are mixed with 3 parts of metallic sodium, and distilled under ordinary pressure, the operation being repeated with the whole or part of the distillate if necessary. Again, 1000 parts of American wood oil are boiled for an hour with 5 parts of caustic soda and 30 parts of alcohol, the latter being eliminated by distillation or washing, and the remainder distilled *in vacuo* after saponification with 2 parts of a liquid alloy of sodium and potassium. In a third example, 1000 parts of Polish pine oil are heated with 5 parts of quicklime, and afterwards distilled from 1½ parts of metallic calcium *in vacuo* or under ordinary pressure.

Dry Distillation Turpentine.—Sundvik publishes in a French journal some notes on the turpentine oil obtained by dry distillation, and known as "pine essence". He points out that whilst pure steam-distilled turpentine oils contain traces of a substance which gives the characteristic blue reaction with tincture of guaiacum, the oils obtained by the dry distillation of the resinous woods do not give this reaction. Further, the hydrocarbons of genuine turpentine deflagrate with iodine, whilst those of the dry distillation product, being far more fully saturated, do not produce this effect. From pure Finnish turpentine the author has isolated a small quantity of terpineol, and also 0·3 per cent of guaiacol. The author has examined seventeen samples of this dry distillation turpentine, and found their optical rotation to vary between + 9·7° and + 17·03°. The distillation temperatures of the "essence of pine" are higher than those of the pure turpentine, the greater part distilling between 160° to 170°, as against 155° to 162° C. for the ordinary spirits of turpentine.

Dry Distillation of Turpentine from Resinous Woods.—Resinous woods are distinguished from hardwoods in yielding a much larger percentage of oils when distilled. Some of these oils exist naturally in the wood, while others are derived from the breaking up of natural resins. When wood is gradually heated as in destructive distillation, and the temperature in the retort rises above 100° C., these oils mixed with water begin to pass over or distil, and continue with rising temperature until the distillation of the wood is complete. The oil passing from the retort at any moment may be different from that which passed previously and from that which follows it, so that in practice the distillate is a mixture of compounds having closely related chemical and physical properties, and this mixture increases in density and

the boiling-point rises with the temperature in the retort. Below the temperature of 250° C. the oils are almost colourless, and there is but little if any breaking up of the natural resins, those that have distilled being naturally in the wood. When, however, the temperature in the retort rises above 200° C., the wood substances begin to char, giving to the products their characteristic smoky odour. Consequently, in order to obtain a turpentine free from this odour the temperature of the retort must not rise above 200° C., until the turpentine is completely distilled. At approximately 250° C., or above, the lighter resins begin to break up, yielding oils which boil at from 97° to 250° C. When the temperature in the retort rises above 300° C. the heavy resins or rosin breaks up, yielding 3 to 7 per cent of light oils, known commercially as "rosin spirits" or "pinoline," boiling at from 97° to 250° C.; 75 to 85 per cent of heavy oils, boiling at from 250° to 450° C., known as "rosin oils," and water containing about 1 per cent of acetic acid. The oils distilling above 200° C. are contaminated by products derived from the breaking up of the wood substance, and these products mask especially the odour of the oils specified, so that they do not have the characteristic rosin-oil odour. By proper methods of treatment and fractional distillation oils of different physical and chemical properties may be obtained, and a number of such oils are on the market under various trade names. Some of these oils have not yet found a regular sale, however, owing to the fact that their composition is not definitely known.

Rosin Spirit.—This product has a specific gravity ranging from 0·856 to 0·883, and a boiling-point varying from 80° to 250° C. It has a peculiar odour, and, with the exception of wood turpentine, is the best substitute known for spirits of turpentine, being much used in the manufacture of the cheaper grades of varnish and as an illuminant. It contains as a characteristic constituent heptane (C_7H_{21}), which boils at 103° to 140° C., has a specific gravity of 0·8031 at 20° C., and absorbs oxygen readily. [This substance has already been described (pp. 139-40), as have the rosin oils, but they are mentioned here to complete the range of products from the low temperature distillation of resinous wood. The data are those of the U.S.A. Forestry Department.]

Rosin Oils.—Crude rosin oils have specific gravities varying from 0·960 to 1·0, while the refined oils vary from 0·960 to 0·990 and boil at from 300° to 400° C. They are largely used in the preparation of axle grease and other low-grade lubricants; also in the manufacture of printing inks, leather dressing, and cement, and as an adulterant for other oils.

Bilfinger Process for Distilling Turpentine.—This is a retorting process. Pine sawings, chips, or sawdust are put into a retort, fitted with suitable condensers, and distilled with superheated steam and fire. One cord of pine-wood takes thirty-six hours to work through, and it gives 25 to 40 gallons of No. 1 turpentine, 15 to 20 gallons of No. 2 turpentine, 30 gallons of tar, 15 gallons of creosote,

and 25 bushels of charcoal. The arrangement of plant is such that the turpentine is easily separated from the tar and creosote. The temperature at which the process is worked is 500° F. It is claimed that a water-white turpentine, equal to the ordinary spirits of turpentine, can be made. The No. 1 grade averages 91 to 95 per cent pure turpentine, and completely evaporates from a sheet of paper, and so does all that the old turpentine will do. The No. 2 grade is not of so good a colour, but is said to be suitable for dark-coloured paints. The tar and creosote are marketable products. From a twelve-retort plant there can be obtained 1000 casks of turpentine per year.

Pine-Wood Distillation in the U.S.A.—A report of the U.S. Department of Agriculture supplies the following figures, showing the quantity of pine distilled and the products. The total amount used by the fifteen operators reporting was 16,969 cords, with a value of $42,805. The products differed, of course, from those of hardwood distillation, in containing a large amount of tar and turpentine, but no alcohol. Much less charcoal is obtained from pine than from hardwood, the average relative proportions being approximately 350 lb. per cord, as against approximately 700 lb. per cord. Tar, a by-product in hardwood distillation, is one of the major products of pine distillation. The average price of pine-wood per cord is also lower. The number of stills was fifteen, and 16,969 cords of wood were used, valued at $42,805. The products comprised 300,106 bushels of charcoal, 362,500 gallons of tar, 434,780 gallons of oil, 238,180 gallons of turpentine.

The Properties and Uses of Steam-Distilled Wood Turpentine.—*Long Leaf Pine Oil*, from the *Pinus palustris* or long leaf pine, the tree known to British carpenters as pitch pine, is obtained as a by-product in the extraction of turpentine from lightwood by means of steam. It merits consideration for its own intrinsic character, not because it is a new product; as its uniformity, many uses, and the large production indicate that it is a valuable source of terpene derivatives. The statements here refer only to the steam-distilled product. The rosin-bath process and the destructive distillation systems give fractions with somewhat similar properties, but in the one case they are contaminated with products of rosin distillation and in the other with creosote compounds.

A few years ago, the sale of this oil was almost negligible, and the greater portions of those fractions of the distillate which contained the oil were thrown away. To-day the purified product is sold regularly in car-load lots. *It will dissolve any of the ordinary varnish resins cold, whereas in the usual methods of manufacturing varnishes the resins must be melted before they dissolve properly.* It is valuable in varnish works for washing filter cloths. It is one of the best solvents for rubber. It can be added to a nitrocellulose lacquer dissolved in amyl acetate without precipitating the nitrocellulose. It is not a rapid hard drying oil, and so is used in coating insulated

cables [as a solvent ?]. The high price of oil of camphor, and the more stringent laws regarding the use of benzine, have led to the substitution of pine oil almost exclusively for these two products in the manufacture of metal polishes. Properly refined it has a pleasant odour which leads to its use (1) by the essential oil trade and (2) soap makers for perfuming cheaper soaps. Its chief constituent is terpineol.

This experiment was repeated, using a sample of long leaf pine oil, of which nearly the whole distilled at 216° to 218° C. 100 grammes of this oil heated for one hour with 400 c.c. of dilute sulphuric acid (1 : 2) and then distilled with steam and dried over sodium, gave 85 c.c. of oils volatile with steam. On redistillation the following fractions were obtained: 5 c.c. at 165° to 175°; 56 c.c. at 175° to 180°; 6 c.c. at 181° to 185°, and 15 c.c. at 186° to 192°. The largest fraction had a specific gravity of 0·860, and evidently consisted essentially of terpinene. These results agree quite closely with Wallach's from pure terpineol. The specific gravity, index of refraction, and boiling-point, its absorption of bromine in quantity corresponding to a dibromide, the formation of a nitrochloride, nitropiperidide and nitranilide, the formation of terpinene by dehydration, and the easy conversion and large yield of terpin hydrate, leave little doubt that the essential constituent of long leaf pine oil is a terpineol and is probably the optically active lævo modification of a-terpineol (Δ-p-menthenol (8)) boiling at 217° to 218° C.

This seems to be the first recorded occurrence of terpineol in any member of the pine family. Even in this case it was obtained not from the living tree but from light-wood, i.e. from portions of the tree which had been cut at least three years and were very resinous. It is the common belief of those familiar with light-wood that its resinous content increases regularly from the time it is cut from the tree or from the death of the tree. If any such action occurs the appearance of terpineol here would seem quite natural, as its formation from pinene requires only the addition of one molecule of water accompanied by splitting the tetra ring of pinene. The investigation of this oil is being continued.

As it comes to market, it is either clear and water-white, containing 3 or 4 per cent of dissolved water, or it may have a very faint yellow colour and be free from dissolved water. The specific gravity ranges from 0·935 to 0·947, depending on freedom from lower boiling terpenes. A good commercial product will begin distilling at about 206° to 210°, and 75 per cent of it will distil between the limits 211° to 218°, and 50 per cent of it between 213° to 217°. A sample having a density of 0·945 to 15·5° showed a specific rotation of about $[a]_D^0$ —11° and an index of refraction of N_D 1·4830. In fractional distillation of the oil the specific gravity of the various distillates rises regularly with increasing temperature, becoming steady at about 0·947 at 217°.

If the oil consists essentially of terpineol, $C_{10}H_{18}O$; it should be

easy to convert it into terpin hydrate, $C_{10}H_{20}O_2 + H_2O$, by the method of Tiemann and Schmidt. The conversion was found to proceed easily when the oil was treated with 5 per cent sulphuric acid, either with or without admixture with benzene. If agitated continuously, the reaction is complete within three or four days. If, on the other hand, the mixture is allowed to stand quietly, the formation of terpin hydrate extends over several months and produces most beautiful large crystals, which, without recrystallizing, melt at 117° to 118° C. When recrystallized from ethyl acetate they melt at 118° C. Yield, about 60 per cent of the theoretical. This forms such a simple, cheap and convenient method of making terpin hydrate that it will doubtless supersede the usual manufacture from turpentine, alcohol and nitric acid, and instead of terpin hydrate serving as raw material for the manufacture of terpineol, as heretofore, the reverse will be the case.

Terpineol Nitrosochloride.—This compound was made in the usual manner from amyl nitrite, glacial acetic acid, and hydrochloric acid. The yield was good, and the product, after crystallization from ethyl acetate, proved to be very stable. Melting-point, 101° to 103° C.

Terpineol Nitropiperidide.—This compound was made from the nitrosochloride and piperidine according to Wallach's method. The once recrystallized product melted at 158 to 159° C. and formed well-shaped crystals from methyl alcohol.

Terpineol Nitranilide was made from the nitrosochloride and aniline dissolved in alcohol. On dilution of the reaction mixture with a little water good crystals of the nitranilide were obtained.

Dehydration Products.—Wallach found that when 25 grammes of terpineol were heated with dilute sulphuric acid, there resulted 16 c.c. terpinene and cineol boiling at 177° to 180° C., 4 c.c. boiling at 181° to 185° C., and 1 c.c. boiling at 185° to 187° containing terpinolene.

Pitch and Tar.—The residues from the purification of turpentine oleo-resin may also be treated in a pitch furnace. The furnace is a truncated receptacle, 3 feet high by 13 feet in diameter at the base and 20 inches in diameter at the top. The furnace is built of brick and surrounded by a thick mass of masonry. The ashes left on the sole are removed and the vent plugged during each operation. The sole is concave and has, in its centre, a small reservoir, corresponding with a cast-iron pipe, leading the pitch or tar into a reservoir; water and sand are deposited at the bottom of the receiver. In making pitch a layer of wood is placed on the sole of the furnace to prevent the exit pipe being choked. The furnace is then filled with the purification residues of the turpentine, leaving the least amount of vacant space possible. The door is closed with bricks and luted with clay. The furnace is lighted from the top. The slightest current of air from the lower region of the furnace burns the mass to ashes. Therefore small cracks are carefully luted with clay. When the furnace is well lighted and the fire has descended far enough the upper orifice is closed by a cast-iron lid which is covered with earth. The heat gradually gains ground and the resin-

ous-matter sweats before being reached by the fire, and forms in the reservoir a mass of soft pitch, which is either put on the market as it is or distilled like turpentine, when it yields a brownish-red spirit and a residue of hard pitch.

We have seen that the residues on the wire sieves and straw strainers still contain oleo-resin, which may be recovered and made into pitch by a steam jet in an open or closed vessel. *Dromart*, in 1863, designed a high-pressure apparatus which avoids loss. The residues are fed through the door into a cylinder above the grating. The tap is opened and the steam drives out the air through another tap. Steam at 150° C. (4·5 to 5 kilogrammes) is then applied. Extraction is incomplete at a lower temperature, at a higher temperature the rosin distils its spirits. Steam is kept underneath the still. Starting in the beginning at a low temperature a certain amount of products distil below 300° F., but the products *richer* in carbon require a higher temperature, but too great a heat must be avoided as it leads to an increase in the gaseous portion of the distillate at the expense of the valuable products, tar, etc.

Wood tar is manufactured in much the same way as the pitch. The raw material consists of small fragments of broken-up pine-wood. The roots yield more tar than the trunk and the heart-wood more than the sap-wood. Re-charging is done as soon as the workmen can enter the furnace. The heat stored up in the walls of the furnace is thus utilized to stimulate the flow of resin. A stere of wood yields 30 to 40 litres of tar, say 300 to 400 litres for a furnace of 10 steres, yielding only one fire a week. The retorts should not be heated above 350° to 400° C. (662° to 752° F.) if it be desired to get the maximum percentage of acetic acid obtainable. When wood is distilled for gas the vapours from the still are led into a heated generator to undergo what is practically a second destructive distillation. In distilling for gas, for which the wood should be specially dry, the charge is about 112 to 132 lb., yielding about 550 cubic feet of gas in an hour and a half. But in distilling for tar, 1 to 2 cwt. or more are distilled in about twelve hours, burning the gas in the furnace under the retort, the flames circulating round about it. The deep red pines richest in resin are chosen, the old tapped trees yielding the best and largest distillate. The gas from the distilling wood itself is the chief fuel used. For the first twelve hours the heat is kept below 290° C. (544° F.), afterwards raising it to 450° C. (842° F.). The average results from sixteen charges of wood, averaging 4573 lb., were: light oil, density 0·875 to 0·950, 13·8 gallons; pine oil, 0·950 to 1·040, 73·5 gallons; pyroligneous acid, 1·02 specific gravity, 185 gallons; charcoal, poor, 1511 lb. The liquid distillates are allowed to deposit when the oil floats on the acid liquor.

When gas is burnt below the retorts, 8 to 10 cwt. of coal are required to distil a ton of wood, and oak takes about 10½ cwt. to the ton. The small retorts used in the southern states of the U.S.A. are made of cast-iron, the larger ones of wrought-iron or steel.

They vary in size from 5 to 30 feet in length and 3 to 9 feet in diameter and 5 to 30 feet long. The furnace gases are led beneath a brick arch. The oil is distilled down to four-fifths and the residue used for creosoting.

Wood-Tar Creosote.—Creosote is derived from two Greek words, κρεας and σωζω, meaning "flesh" and "I save". It was first discovered in beech-wood tar by Reichenbach in 1833. Of the five new bodies which Reichenbach discovered in wood-tar, and in regard to which Dr. Angus Smith remarks, "people could not find them till long after he died," creosote is the most important.

Creosote may be prepared either from wood-tar or from crude, pyroligneous acid. The tar must be distilled till it acquires the consistence of pitch, and at the utmost till it begins to exhale the white vapours of paraffin. The liquor which passes into the receiver divides itself into three strata, a watery one in the middle, placed between a heavy and a light oil. The lower stratum alone is adapted to the preparation of creosote.

1. The liquor being saturated with carbonate of potash, is to be allowed to settle, and the oily matter which floats at top is to be decanted off. When this oil is distilled, it affords at first products lighter than water containing but little creosote, which are to be rejected, but the heavier oil (with a bad smell and sour-sweet caustic bitter taste which at first is pale yellow but becomes brown by exposure to the air) which follows is to be separated, washed repeatedly by agitation, with fresh portions of dilute phosphoric acid, to free it from ammonia, then left some time at rest, after which it must be washed by water from all traces of acidity, and finally distilled along with a new portion of dilute phosphoric acid, taking care to *cohobotate*, or pour back the distilled product repeatedly into the retort.

2. The oily liquid thus rectified is colourless; it contains much *creosote*, but at the same time some *eupione*, etc. It must therefore be mixed with potash lye at 1·12 specific gravity which dissolves the creosote. The "eupione" floats upon the surface of that solution, and may be decanted off. The alkaline solution is to be exposed to the air till it blackens by decomposition of some foreign matter. The potash being then saturated with dilute sulphuric acid, the creosote becomes free, when it may be decanted or siphoned off and distilled.

3. The treatment by potash, sulphuric acid, etc., is to be repeated upon the brownish creosote till it remains colourless, or nearly so, even upon exposure to air. It must be now dissolved in the strongest potash lye, subjected to distillation anew, and lastly, re-distilled with the rejection of the first products which contain much water, retaining only the following, but taking care not to push the process too far.

In operating upon pyroligneous acid, if we dissolve effloresced sulphate of soda in it to saturation, at the temperature of 267° F., the creosote oil will separate, and float upon the surface. It is to

be decanted, left in repose for some days, during which it will part with a fresh portion of the vinegar and salt. Being now saturated while hot with carbonate of potash and distilled with water, an oily liquor is obtained, of a pale yellow colour. This is to be rectified by phosphoric acid, etc., like the crude product of creosote from tar.

Creosote is apparently composed of 76·2 carbon, 7·8 hydrogen, and 16·0 oxygen, in 100 parts. It is an oily-looking liquid, slightly greasy to the touch, void of colour, having an acrid burning taste, and capable of corroding the epidermis in a short time. It possesses a penetrating disagreeable smell, like that of highly smoked hams, and when inhaled up the nostrils causes a flow of tears. Its specific gravity is 1·037, at 58° F. Its consistence is similar to that of oil of almonds. It has no action upon the colours of litmus or turmeric, but communicates to white paper a stain which disappears spontaneously in a few hours, and rapidly by the application of heat.

It boils without decomposition at 398° F. under the average barometric pressure, remains fluid at 27° C. In distinction from coal-tar creosote, is a non-conductor of electricity, refracts light powerfully, and burns in a lamp with a ruddy smoky flame.

When mixed with water at 58° F. it forms two different combinations, the first being a solution of 1 part of creosote in 400 of water; the second, a combination of 1 part of water with 10 parts of creosote. It is miscible in all proportions with alcohol, ether, acetic ether, naphtha, carbon disulphide, anhydrous glycerine, and with fatty and essential oils, etc., but it is not miscible with liquor.

Creosote dissolves resins and camphor, a large quantity of iodine and phosphorus, as also of sulphur with the aid of heat, but it deposits the greater part of them in crystals on cooling. It combines with potash, soda, ammonia, lime, baryta, and oxide of copper. Oxide of mercury converts creosote into a resinous matter, while itself is reduced to the metallic state. Strong sulphuric and nitric acids decompose it.

Creosote dissolves several salts, particularly the acetates, and the chlorides of calcium and tin; it reduces the nitrate and acetate of silver. It also dissolves indigo blue; a remarkable circumstance. Its action upon animal matters is very interesting. It coagulates albumen, ammonia, fixed alkalies, etc., and prevents the putrefaction of butcher's meat and fish. For this purpose these substances must be steeped a quarter of an hour in a weak watery solution of creosote, then drained and hung up in the air to dry. Hence Reichenbach has inferred that it is owing to the presence of creosote that meat is cured by smoking; but he is not correct in ascribing the effect to the mere coagulation of the albumen, since *fibrine* alone, without creosote, will putrefy in the course of 24 hours, during the heats of summer. It kills plants and small animals. It preserves flour paste unchanged for a long time.

Creosote exists in the tar of beech-wood, to the amount of from 20 to 35 per cent, and in crude pyroligneous acid.

It ought to be kept in well-stoppered bottles, because when left open it becomes progressively yellow, brown and thick.

Creosote has considerable power upon the nervous system, and has been applied to the teeth advantageously as well as to the skin in recent scalds. Its medicinal and surgical virtues have been much exaggerated. Its flesh-preserving qualities have been rendered of little use by the difficulty of removing the rank flavour which it imparts. Ure found the following "constants"—a sample from Zimmer & Co. had a density of 1·054, a north of England sample 1·057 and a boiling-point varying from 370° to 380° F. Morson's creosote (much esteemed) had a density of 1·070 and boiled first at 280° F., but progressively rose in temperature to 420° F., when it remained stationary. The German sample was distilled from the tar of the pyroligneous acid manufacture. "Creosote, I believe, is often made from Stockholm tar" (Ure).

PART III.

SPIRIT VARNISH RESINS AND COLOURING MATTERS.

CHAPTER XIV.

BENZOIN.

Benzoin.—Malay benzoin was known to the Arabs under the name of *Incense of Java*, *Luban Djawi* or *Djaoui*, corrupted into *Ban Djaoui*, hence probably the origin of the word *Benzoin*, corrupted in Great Britain into *Benjamin*. Benzoin is a balsam secreted by a small tree of the Malay Archipelago, that is by one or more species of *Styrax*, a genus giving its name to the natural order *Styraceae*. There are four kinds of the balsam met with on the London market. It is well known that *Styrax benzoin*, Dryander, is the source of Sumatra benzoin, but there is considerable doubt as to the exact source of the other three sorts. Some authors assert that Siam benzoin is produced from a different species from that of Sumatra. Pierre alleges that the species are one and the same, viz. *S. benzoin*, Dryander (*Plagiospermum benzoin*, Pierre). But as a distinction is made in the resin trade between the Malay or Sumatra benzoin, it will be advisable to study the products separately. It may, however, be as well to state at the outset that the Siam resin is the most costly and the most highly esteemed.

1. *Sumatra Benzoin* (Malay synonym, *Menjan*, Indian synonyms, *luban* (bazaars), *hussi*, *shambirani kaminian*) exudes in whole or at least the greater part from *S. benzoin*, Dryander. It is a small tree with oval elliptical or oval oblong leaves, only velvety on their external surface, imbricated, convoluted. The stamens (eight to ten) are shorter than the petals, and the style, with downy filaments, concrescent underneath with the tube of the corolla. The ovary is ovoid, sessile, with three to four incomplete dissepiments, surmounted by a long thin and glabrous style. The ovules, arranged in two series of three, are subascendant and semi-anatropous. The fruit is a spherical, red, pubescent, indehiscent, monospermous drupe, with an external, suberose envelope and bony endocarp. The sessile seed has its external tegument traversed by six longitudinal grooves. It is furnished with a subcorneous albumen and a transversal embryo. This tree may be grown in almost all soils, but it frequents upland, dry, sandy, never flooded ground. It does not appear to go above an altitude of 1000 feet. In low-lying damp ground the trees grow rapidly, but only yield inferior resin. It does not grow on marshy, flooded ground nor on limestone. Reproduction is by seed sown in nurseries and transplanting the young trees and slips growing round about the

adult trees, which are separated from the mother plant and transplanted into suitable soil, shading them from the sun during the early stages of development, and protecting them from the invasion of an undergrowth of brushwood, which would stifle them. The

Fig. 23.—*Styrax benzoin* (Dryander, after Greshoff). 1, branch and inflorescence; 2, entire fruit; 3, fruit, the epicarp of which has been cut to expose bony endocarp.

cultivation of the tree therefore presents no great difficulty. The trees are exploited in their seventh year during the dry season. The incisions are made in the trunk by means of a sort of hatchet which the Malays call a *parang*. They are scarcely incisions but deep triangular wounds or takoli, the dimensions of which do not exceed 1

centimetre; they pass through the bark and enter the wood. When a tree is tapped for the first time nine cuts are made arranged three by three along three vertical lines, or to be more exact, along three equidistant genetrices drawn on the surface of a cylindrical trunk. On each of these verticals a first cut is made 4 centimetres from the ground, a second the same distance above, and a third at the same distance still higher up. The bark is scraped and suitably cleaned in the intermediate spaces. After eight days a yellowish liquid quickly passing to brown issues from the wounds. The slight exudation, remaining viscous a long time, covers the cuts and the neighbouring bark. It takes two months to harden so far as to be capable of collection. But the resin of the first exudation is valueless and is not collected, it is detached by the parang whilst at the same time three new cuts are made in the same verticals 4 centimetres above, then a fourth 40 centimetres above the highest of the three. After another three months, a new series of cuts 4 centimetres above the four preceding and 40 centimetres above the fourth, and so on every three months. When the first three verticals are filled, new sources are attacked either to the right or to the left, following the same method, which may be varied, still retaining the same principle. In the first six months following the beginning of the tapping the scanty product is of mediocre value. But afterwards for three consecutive years the maximum yield is obtained, which corresponds with the middle age of the life of the tree. Then production decreases, the tree becomes exhausted and dies after seventeen or nineteen years' existence. When the benzoin is poor it is so fluid that it flows down the trunk of the tree to the ground. Good qualities are known by the exudation being thick and viscous and adhering to the bark around the incisions in fine, bright yellow masses. It is then collected every three months, as benzoin does not lose its sticky nature until after two months' exposure to the air. The pieces are detached with a parang or a bamboo blade, working it from below upwards, so as to avoid peeling the bark with the parang; it is blackish and very impure. In a well-managed plantation a tree may yield more than three kilogrammes of benzoin in each collection. The product after a fresh assortment is packed in barrels made from bark and called kepock menjan, which are covered with the wide sheaths of palm leaves.

Varieties of Malay Benzoin.—(1) Sumatra or Padang benzoin, which is the most esteemed, either, as is claimed, because it contains more benzoic acid than other sorts or because it is more pure, being collected with greater care; (2) Palembang benzoin, the low value of which is due partly to sophistication by Chinese; (3) Penang benzoin, the importation of which into London is comparatively recent, say sixty years ago, whilst the two former sorts have been known there for more than two centuries. Moreover, Penang benzoin appears so different from the other two by its characters and properties that Hanbury attributed its botanical origin to a particular species, the *S. Subdenti-*

culata, Miquel. But nothing has since occurred to confirm this assertion. The chemical composition and properties of benzoin in general are given under Siam benzoin.

Siam Benzoin, the source of which is hardly known, is, according to Pierre, the *Styrax benzoin* (Dryander) [*Plagiospermum benzoin* (Pierre)], cultivated in Sumatra and Java. The benzoin tree is quite common in the kingdom of Luang Prabang, where the natives call it *hoc nham*. It is especially abundant in the valley of Nam-hou, and more particularly in that of its affluent, the Nam-bac. Almost the whole of the production, sometimes very plentiful, is exported at Bangkok. The tree is rarely found in Cambodia. The benzoin tree, if it has not to be introduced, at least requires to be propagated in French Indo-China. It might be cultivated as in Sumatra, by seeds, and by the numerous slips which the adult plant bears upon its large roots. The Siam method of collection is unknown, except in so far that it is after the fall of the leaf, in April or May, that the Siamese make deep longitudinal incisions through which the resinous liquid sweats, which soon concretes into more or less bulky masses. Grand says the Laotians rest content with incising the trunk of the tree. Siam benzoin consists of amygdaloid tears cemented together by a brown translucent paste. As to the tears which form so many almonds in the body of the mass, they are more or less coloured, sometimes they appear reddish, this tint being due to the action of the air before being embedded in the paste. The best qualities of benzoin show this amygdaloid appearance. Benzoin exhales a savoury odour approaching that of vanilla. It melts on heating, emitting a strong odour. It is very soluble in alcohol and ether. It contains, besides a minimum proportion of essential oil, two acids, benzoic acid and sometimes cinnamic acid. The first occurs alone in Siam benzoin, but cinnamic acid is characteristic of Sumatra benzoin. Benzoic acid is got from it in two ways; when benzoin is heated in a vessel surmounted by a cone of cardboard (Fig. 25), the acid sublimes as light crystalline flakes, which were formerly termed *flowers* of benzoin. Another process, due to Scheele, consists in boiling the benzoin with milk of lime, and in concentrating it by evaporation, and precipitating by hydrochloric acid. The benzoic acid separates, and is purified by crystallization in boiling water. Siam benzoin is highly valued in perfumery. Its price seems to have diminished greatly, whilst the exports have simultaneously decreased. In 1889 the quantity put on the market was 521 piculs, worth 62,812 dollars, which makes (the picul being 133 lb.) about 69,293 lb., worth £12,560, or say 3s. 7d. the lb. In 1890, owing to the extreme depreciation of benzoin on the European market, the value of the exports only amounted to 46,780 dollars. Finally, in 1896, the French Consul at Korat reported benzoin as being worth only 146 francs the 100 kilos, say about 10d. the lb.; the exportation was 160 piculs, worth 8742 ticaux the beal, being about 1s. 3d. of our money.

Sumatra benzoin contains three different resins; moreover it

ontains a small quantity of an essential oil and a mixture of enzoic acid and cinnamic acid or cinnamic acid alone. Kolbe nd Lautemann met with some specimens of benzoin which did ot contain benzoic acid. From one sample of the best quality rought from Sumatra they extracted an acid altogether different :om benzoic acid, fusible in hot water and giving oil of bitter lmonds when oxidized by potassium permanganate and supposed ɔ be identical with alpha toluylic acid, which Müller and Strecker btained by heating vulpinic acid with baryta. Tschirsch analysed sample of Sumatra benzoin. He gives the following particulars f his methods, results, and deductions. It gave ash 0·01 per ent; distilled with steam it gave traces of styrol and a mixture f cinnamic and benzoic acid, which were identified by conversion ıto the ethyl ether, fractionation, and saponification. The benzoin ʻas dissolved in ether and shaken with 4 per cent soda lye.

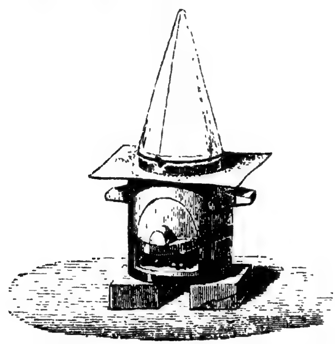


FIG. 25.—Sublimation of Benzoic Acid.

.n oil remained dissolved in the ether which was extracted there-·om by sulphite solution and gave a small amount of benzaldehyde nd some time afterwards colourless crystals, melting-point 44° C., ʻhich on saponification gave cinnamic acid, melting-point 133° C., and innamic alcohol, boiling-point 250° C., and which on analysis ʻas recognized as styracin ($C_{18}H_{16}O_2$). Found: C = 82·1 per cent; I = 6·3. Calculated for $C_{18}H_{16}O_2$: C = 81·81 per cent; H = 6·06 ıer cent. When all the stryacin was crystallized out the remaining il was fractionated in a stream of CO_2. In the first fraction two ;rammes (boiling at 78° to 80° C.) benzol was found and identified by he nitrobenzol and aniline reaction; in the second fraction (80° o 150° C.) traces of styrol. The higher fractions were decomposed ınd contained cinnamic acid, benzyl ester and benzoic acid benzyl ster. When the oil after the separation of the benzaldehydes and the tyracins was distilled with steam a heavy oil remained in the flask, ıhenyl propyl cinnamate, $C_{18}H_{18}O_2$, which on saponification gave innamic acid, melting-point 133° C., and phenyl propyl alcohol,

boiling-point 235° C. Found: C = 81·3 per cent; H = 6·6 per cent. Calculated for $C_{18}H_{18}O_2$: C = 81·2 per cent; H = 6·76 per cent. This ester does not decompose on volatilization. If hydrochloric acid be added to the ethereal solution extracted with soda lye, and filtered hot, much benzoic acid and a little cinnamic acid separates out on cooling. The crystals which, after standing for a day, were filtered from the solution are taken up with ether, and the ether treated with sulphite solution. Crystals separated from the sulphite solution which gave all the reactions of vanillin. Found: C = 63·7; H = 5·5. Calculated for $C_8H_8O_3$: C = 63·15; H = 5·26. The substance which imparts the smell to benzoin had still to be determined. Styracin and phenyl propyl cinnamate are odourless or almost odourless, and vanillin has a peculiar smell of its own which in nowise resembles benzoin. Tschirsch, however, was never able to obtain phenyl propyl cinnamate odourless. Yet Miller says that when pure it is completely odourless. For the estimation of the free acids in Sumatra benzoin the benzoin was dissolved in ether and the solution strongly agitated with 1 per cent soda solution. To the extract NaCl was added and the mixed acids, melting-point 125° C., gave the benzaldehyde reaction with permanganate, and the benzoic acid and cinnamic acid were separated therefrom. The ethereal solution of the benzoin was shaken with water of 50° C., filtered and neutralized with soda, and gave a fluid which, evaporated and mixed with HCl, only left the acid mixtures.

These tests prove that benzoin contains no other free acids except benzoic acid and cinnamic acid, except in minute quantity. The resin freed from free acids, esters, hydrocarbides, and aldehydes were now saponified by potash and steam. To the saponified fluid strong potash was added, and after adding potash in sticks was evaporated by direct fire heat. There separated, on the addition of a few drops of ether, silky needles of a colourless compound, the potassium salt of a resin alcohol of the benzo-resinols. On the addition of HCl to the brown solution benzo-resino tannol was precipitated, from which benzo-resinol was extracted by concentrated alcoholic KHO. Benzo-potassium resino tannol is precipitated, which with HCl gives benzo-resino tannol, likewise a resin alcohol.

The two alcohols may be roughly separated by treating the mixture with lime.

Calcium benzo-resino tannol is insoluble in alcohol. Benzo-resinol, melting-point 274° C., is insoluble in water, soluble in alcohol, ether, chloroform, aceton toluol, acetic acid, and ammonia; insoluble in petroleum ether.

The alcoholic solution reacts neutral. Benzo-resinol dissolves to a deep red-coloured solution in concentrated H_2SO_4, and this is known as the sulphuric acid test for benzoin. It crystallizes from ether and acetone in fine needles, from strong or dilute alcohol in tufts. The potash solution, salted out by strong potash, gives fine needles of potassium benzo-resinol. Very strongly heated it sub-

limes in needles. The deep red solution in concentrated sulphuric acid shows a broad band between $\lambda = 0{\cdot}555$ and $\lambda = 0{\cdot}510\mu$, which on increasing the thickness of the plate gives a broad band of blue with absorption of blue and violet. With the Liebermann cholesterol reaction benzo-resinol gives a rose-red coloration which passes from blue to green, and with the Salkowski-Hesse reaction the chloroform is coloured blood-red. Benzo-resinol gives the phytosterin reaction. The analysis of benzo-resinol gave the following results. Found mean of five analyses: C = 76·5; H = 10·6. Calculated for $C_{11}H_{20}O_2$: C = 76·8 per cent; H = 10·4 per cent; the molecular weight estimation with phenol gave 244 and 249. The formula $C_{16}H_{26}O_2$ requires 250. Potassium benzo-resinol is very readily decomposed. Analysis shows it to be a monopotassium compound, 13·5 per cent. Benzo-resinol absorbs bromine, but can neither be acetylated nor benzoylated. However, Tschirsch prepared methyl and ethyl ethers from it. The methyl ether, melting-point 174° C., by boiling with alcoholic (methyl) potash a benzo-resinol solution in methyl alcohol, containing methyl iodine, crystallizes out on adding a few drops of water to the alcoholic solution and responds to the formula $C_{16}H_{25}O_2CH_3$. The ethyl and isobutyl ether were also prepared. Finally, to combine the benzo-resinol with cinnamic acid a solution of the two in ether was saturated by HCl gas, and the excess of acid neutralized by dilute soda solution. The benzo-resinol cinnamate, melting-point 206° C., so obtained dissolves in alcohol, ether, chloroform, benzol, but is insoluble in water and petroleum is ether left on saponification, cinnamic acid and benzo-resinol, and responded to the formula $C_{16}H_{25}OC_9H_7O_2$. Found: C = 78·2 per cent; H = 8·8 per cent. Calculated: C = 78·9 per cent; H = 8·4 per cent. The compound did not yield crystals. Tschirsch claims it as the first artificially prepared resin ester, the first synthetic resin. The second resin alcohol obtained by the saponification of the mixture of resin esters is benzo-resino tannol or Sumatra-resino tannol. It is prepared ash free from the potassium compound by precipitating the solution of the same by hydrochloric acid. Like all other resino tannols it does not crystallize; it forms a dark brown powder, slightly soluble in alcohol, scarcely soluble in chloroform, benzene, or toluene. Its potassium compound is precipitated from its alkaline solution by strong potash. The deep brown-red solution in concentrated sulphuric acid shows an absorption in the blue of three dull bands; a $\lambda = 0{\cdot}600\mu$ at $\lambda = 0{\cdot}550$ and $\lambda = 0{\cdot}500\mu$.

The resino tannol gives with iron chloride a brown-black, with lead acetate a pale brown, and with potassium pyrochromate a red-brown precipitate. It is blackened by HCl; it also contains a tannin compound, a tannol. Its melting-point could not be determined. Sumaresino tannol gave the following analysis. Found: C = 72·24; H = 7·08. Calculated for $C_{18}H_{20}O_4$: C = 72·00; H = 6·66. The formula $C_9H_{10}O_2$ also applies. Sumaresino tannol forms an easily decomposable monopotassium compound $C_{18}H_{19}O_4K$ which is pre-

cipitated from the alcoholic tannol solution by alcohol potash. It is readily decomposed on purification, yielding a molecule of water. Found: K = 10·91. Calculated for $C_{18}H_{19}O_4K$: K = 11·58 per cent. Sumaresino tannol absorbs bromine left in contact with nitric acid; it is nitrated forming picric acid with dilute nitric acid, it is oxidized into red-brown phobaphenic oxidation products. Heated with ethyl iodide it forms an ethyl ether, and contrary to tannol it is hardly soluble in alcohol but readily soluble in ether. It responds to the formula $C_{18}H_{19}O_4 . C_2H_5$. Found: C = 73·3; H = 7·46. Calculated for $C_{18}H_{19}O_4 . C_2H_3$: C = 73·17; H = 7·31. The potassium melt only gave fatty acids (butyric acid), likewise phenol, and identified by analysis protocatechuic acid. Sumaresinol belongs therefore to the non-glucosidic protocatechuic tannoids. Hlasiwetz and Barth obtained from a benzoic potash melt protocatechuic acid and volatile fatty acids coming from the resino tannol (burnt catechin), *p*-oxybenzoic acid, and an oxidation product of benzoic acid. Hlasiwetz apparently wrought on Siam benzoin, but benzoic acid was not obtained from the melt when the resin esters were acidulated. But the potassium melt of Sumatra benzoin contains benzoic acid, and cinnamic acid it is known in this operation splits up into acetic acid and benzoic acid. The saponification of the pure resin shows therefore that benzoin contains two bodies of an alcoholic natural benzo-resinol and sumaresinol. So as to establish which of the acids paired with the alcohol in the formation of esters the resin ester or resin was isolated perfectly free from free acid. The ethereal solution of the benzoin was precipitated by petroleum ether, the precipitate dissolved in ether and again precipitated by petroleum ether, then it was dissolved in ether and agitated with 1 per cent soda solution to separate free acid. The ester mixture so obtained was completely neutral. It exhibited the property of all other isolated resins, that of being obtained, when softened, in long shining threads, and on saponification becoming harder and finally pulverizing. The saponification is finished when the mass on heating is no longer soft but yields a granular powder. Iron chloride only gives a green coloration, no precipitate. The resin so obtained behaves like all other tannol resins and is readily identified by this reaction. If the resin be saponified with potash under a reflux condenser, the solution acidulated, filtered hot, cooled, silky crystals soluble in hot water separate, which may be obtained colourless by filtration through bone-black, melting-point 133° C. Analysis shows it to be cinnamic acid. Found: C = 73·02; H = 57. Calculated for $C_9H_8O_2$: C = 72·97; H = 5·41. On hydrolysis the resin esters are also split up into cinnamic acid. The combined cinnamic acid separated by HCl was dissolved in dilute potash and at a boiling heat. Strong potash added, crystalline needles separated out on cooling, recognized as potassium benzo-resinol. On acidulating with HCl they left benzo-resinol, melting-point 273° C., identified by its reactions and its elementary analysis. From the filtrate from the potassium benzo-resinol HCl separated sumaresino-

tannol $C_{18}H_{20}O_4$, which, purified and analysed, was identical with siaresino tannol (described below). To sum up, the resin ester mixture of Sumatra benzoin consists of benzo-resinol cinnamate and sumaresino tannol cinnamate. These constitute the greater part of the mass of benzoin. All other bodies isolated from Sumatra benzoin are only present in small quantities. It follows, therefore, that the α, β, γ and δ resins of the older authorities, the collection afforded by the benzaldehyde reaction with permanganate, are nothing but more or less strongly saponified mixtures of esters. It will be readily understood, therefore, that all these resins when boiled with caustic soda can be changed into the γ-resin, the form the most strongly saponified resin assumes. To establish the proportion in which the two resins are in the ester mixture a weighed amount was taken, 27·1, and saponified; the two resin alcohols were extracted by concentrated potash and weighed, the cinnamic acid was estimated as loss and by titration. The results were:—

Benzo-resinol	5·2
Sumaresino tannol	64·5
Loss cinnamic acid	30·2
Cinnamic acid by titration	32·9

9·4 grammes cinnamic acid should have been obtained from the ester (27·1 grammes); by titration 8·9 was found.

The ester mixture therefore consists of

	Per cent.
Sumaresino tannol cinnamate	92·6
Benzo-resinol cinnamate	7·4

Tschirsch, in his analysis of Siam benzoin, followed the same methods as were used for Sumatra benzoin. Siam benzoin contains little or no ash. It dissolved, with the exception of plant debris, completely in ether. The ethereal solution was energetically shaken with very weak caustic soda, 2 per cent, and the aqueous solution separated; the procedure repeated with highly dilute soda and then with water. The ethereal solution gave with sulphite solution no aldehyde. Benzaldehyde, however, occurs in Siam benzoin. On evaporating off the ether a small amount, 0·3 per cent, of an oily fluid remained, from which, after exposure to intense winter cold for a week, no styracin separated, so that body is absent from Siam benzoin. Benzo, styrol, and phenyl propyl cinnamate were not found. It, however, contained a benzoate. Benzoic acid, melting-point 121° C., but no cinnamic acid, was obtained on saponification of the fraction which distils over at 285° C. Combined therewith was a substance which gave the benzaldehyde reaction with permanganate as well as cinnamic alcohol and benzyl alcohol, both of which yield benzaldehyde on oxidation. The amount was not sufficient to determine the proportion. To isolate the substance 10 kilogrammes must be taken. Some light is required as to the occurrence of this substance, as cinnamate, reacting with permanganate in Siam benzoin, which contains no cinnamic acid, neither free nor combined as ester.

The lye obtained by agitating the ethereal solution of benzoin after drawing off the ether was treated with hot HCl. The whole of the resin is separated and filtered hot. Crystals separate from the cooled filtrate, melting-point 121° C., with the properties and elementary analysis of benzoic acid which thus occurs in the free state. The crystals did not respond to the benzaldehyde reaction. Free cinnamic acid is also present in traces. By the above method of working it is not quite demonstrated what substance the saponification begins to act upon. It was, therefore, advisable to determine definitely whether benzoic acid occurred either free or combined in Siam benzoin. The ethereal solution of benzoin was extracted with 0·25 per cent soda solution and decomposed with hot HCl. Benzoic acid, melting-point 121° C., crystallized out on cooling. No better result was obtained when from the soda solution acidulated by HCl the small amount of resin left in solution was precipitated by carbonic acid. The separated acid in all precipitates, by its melting-point reaction and analysis, was identified as benzoic acid. The acid solution after the crystallization of the benzoic acid was shaken with ether, the concentrated ethereal solution shaken with sulphite solution, the latter shaken with ether to free it from absorbed benzoic acid, and sulphuric acid added. The acid solution gave a vanillin ether which purified by sublimation was recognized by its crystalline form and its reactions.

The resin left after supersaturation of the alkaline solution by acid in the hot state and completely freed therefrom by washing and by precipitation from all separated benzoic acid, may be regarded by analogy as the product of the saponification of a resin ester mixture by soda solution analogous to that obtained from Sumatra benzoin. On cooling the hot acidulated saponified fluid silky crystals separated, with a melting-point of 121° C., which did not give the benzaldehyde reaction and which by properties and analysis was found to be benzoic acid. This substance is here also a resin, and benzoic acid is one of the substances coupled or paired in the ester. This explains the abundance of benzoic acid which benzoin yields when this resin is saponified by alkalis. The other substance coupled or paired in the resin ester and cedes itself to the above methods—extraction by lime or strong soda with addition of ether. It separates into two alcohols, one of these, by its reactions, melting-point 272° C., and elementary analysis, is recognized as benzo-resinol, the other, though it only gives with iron chloride and potassium pyrochromates a darker colour (iron chloride, black-brown), and no precipitate, is a new resino tannol termed siaresino tannol. Siaresino tannol is purified by repeated precipitation from its alkaline solution by HCl or lead acetate. It dissolves in the same solvents as sumaresinol and gave the following analysis. Found mean of nine analyses: C = 70·01; H = 6·91. Calculated for $C_{12}H_{14}O_3$: C 69·9; H 6·8. The potash determination in the dry potassium compound gave K · 15·5, 15·6. Calculated for $C_{12}H_{13}O_3K$, 15·9 per cent. Fresh precipitated potas-

sium siaresino tannol contains 1 molecule of water of crystallization, $C_{12}H_{13}O_2(OK)H_2O$. Siaresino tannol can be acetylated (in tube with acetic anhydride). The acetyl derivative, almost insoluble in alcohol and therefore easily extracted from the unacetylated tannol, gave the following analysis. Found mean of two analyses: C = 67·49; H = 6·38. Calculated for $C_{12}H_{13}O_3$: C = 67·7; H = 6·4 per cent. A monoacetylated derivative is thus formed. Siaresino tannol therefore contains a hydroxyl, and it may be given the formula $C_{12}H_{13}O_2OH$. With concentrated nitric acid it yields picric acid; with dilute nitric acid, red-brown phlobaphene analogous to that from sumaresino tannol. To prove in a stringent manner that the bulk of the resin in Siam benzoin consisted of a mixture of resin esters, the resin was isolated in a pure form. The ethereal solution of the resin was repeatedly precipitated by petroleum ether, and the last traces of free acid removed by 0·1 soda solution, finally by washing water. The neutral resin dissolves completely in ether. The ethereal solution can also be acted on direct by soda solution without precipitation by petroleum ether.

The resin ester mixture which dissolves in the usual solvents, but not in petroleum ether, here again exhibits the property when melting of being capable of being drawn out into silky strings. A brown solution is obtained by saponification of the ester mixture by potash solution which is precipitated boiling hot by HCl and filtered hot. Silky benzoic acid crystallizes from the cold filtrate, melting-point 121° C. They did not give the benzaldehyde reaction with permanganate and were perfectly free from cinnamic acid, and on analysis were identified as benzoic acid. The hydrochloric acid portion was treated as described under Sumatra benzoin. It gave, on the one hand, benzo-resinol identical with that from Sumatra benzoin; on the other hand, siaresino tannol, $C_{12}H_{14}O_3$, identical with the above-described sumaresino tannol.

The ester mixture of benzoin consists of resinol benzoate C_8H_{17}—O—O—O—CO . $_{16}H_5$ and siaresino tannol benzoate $C_{12}H_{13}O_2$—O—O—CO . C_6H_5. A quantitative estimation gave

	Per cent.
Benzoic acid	38·2
Siaresino tannol	56·7
Benzo-resinol	5·1

from which it appears the tannol ester is in excess. The ease of saponification of the resin esters varies greatly. The resin ester of Siam benzoin is readily saponifiable, that of Sumatra benzoin with difficulty. The latter is completely saponified by the aid of steam.

According to F. Reinitzer, Siam benzoin exudes from the tree in the form of a milky white fluid. This exudation is produced only after incision, and must be regarded as a pathological product, formed by changes in the protoplasm and not produced from tannin as is generally supposed. Siamese benzoin in tears is distinctly crystalline, melting at 59° C. When these are heated in the

dark at 40° to 50° C., they become dark coloured and amorphous, similar to the basis of the commercial benzoin. The purified benzoin melted at 72·8° C., and was perfectly crystalline; it also became brown on heating. The chief product of Siamese benzoin is the benzoate of a resin alcohol which Reinitzer has termed "lubanol"; it also contains a substance similar to the "benzoresino tannol" of Lüdy, melting at 277° C., but containing a higher proportion of oxygen than the last named. This has been called "siaresinol". A third substance present is an amorphous benzoate. The principal product, "lubanol" benzoate, gives a green colour with ferric chloride, a blue colour with chloral hydrate on heating, and also a coloration with the Liebermann-Salkowski reagent.

Sumatra benzoin also flows from the tree as a milky-white product, and therefore the sumaresino tannol is probably an oxidation product subsequently formed.

CHAPTER XV.

DAMMAR, KAURI, ETC.

Dammar.—This is the name given to more or less allied resins, e.g. East India dammar, Batavian dammar, Sal dammar, Rock dammar. But dammar is more a generic name than a specific name. "Dammar" is, in fact, the Malay term for all gums and all resins which exude from trees and solidify rapidly on exposure to the air. Besides the true dammars, the products of species of *Dammara*, there are met with on the market several varieties of resins derived from very different species of trees which also come on the market as dammar. Thus Indian dammar is derived from the *Shorea robusta*; white dammar is furnished by the *Vateria Indica*, both belonging to the *Dipterocarpaceæ*, whilst black dammar is the product of a *Burseracea*: the *Canarium strictum*. But the origin of dammar is so confused that even the above statements require qualification. Thus included in the genus *Shorea* are several species besides *Shorea robusta* which yield an analogous resin to Indian dammar, and these species are not grown in India (*vide infra*); and this also applies to both the *Vateria* and *Canarium*. Again, in India resins from species of *Gardenia* have been classified amongst the dammars. The true dammars would be resins which flow from the trunk of several species of the genus *Dammara* (*Agathis Salisb* of the family of conifera, the *Dammara alba*, Rumph, the *Dammara orientalis*, Lamb). But these are not the dammars of commerce, nor do they yield Batavian dammar. They have been already described in Vol. II of this treatise under the heading of Manila Copal and Kauri Copal.

The term dammar in Malay has several meanings. It may mean a particular resin or any resin, and as "links" or "torches" or "flambeaux" were made by dipping wood in melted resin, the word came to mean in Malay not only a resin, or all resins, but also a lamp or light. The botanists apply the term dammar resin to the resin obtained from the species of *Dammara* indigenous to Oceania. But British varnish-makers and brokers and "gum" washers apply the term Manila copal to the resin derived from the dammars of Oceania, hence much confusion. The resin derived from the true dammar of the botanists is the varnish-makers' Manila copal, whilst the dammar of the varnish-maker is derived mostly from Dipterocarpus trees, *Shorea*, *Hopea*,

Vatica, Drybalonops, Vateria, Doone, partly from trees of the order *Burseracea* (*Canarium*), partly from guttiferæ (*Garcinia*). The Batavian dammar, the only dammar known to the British varnish-maker, broker, and "gum" washer, is in all probability the product of a *Shorea.* At any rate, as its chemical behaviour to chloral teaches, Batavian dammar is the product of a Dipterocarpus tree

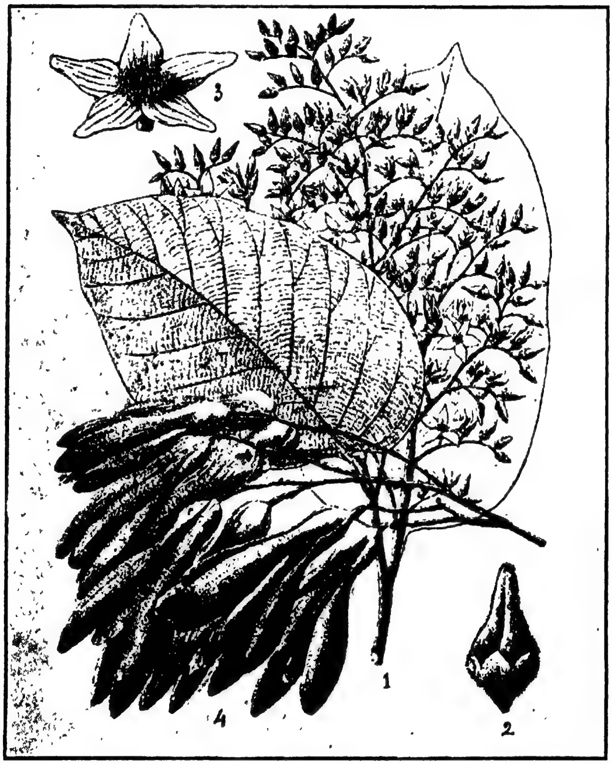


FIG. 26.—*Shorea robusta* (Gaertner), after Brandis and Gilg: 1, branch and inflorescence; 2, floral bud; 3, flower; 4, group of fruits enveloped each by their lobes springing from the calyx.

and not that of a conifer. Wiesner cleared the atmosphere as to its source by declaring that it could not possibly be derived from a dammar tree. Schiffner has found the plant, to which he has given the preliminary name of *Shorea Wiesneri Schiffn.*, MSC., but has up to now published no diagnosis. It is allied to *Shorea selanica*, Blume. In the older woody fibres and in the older bark are found long schizogenous and schizolysigenous resiniferous

channels, the so-called lysigens of Wiesner. The resin is collected in Sumatra as follows: Incisions reaching deeply into the wood, arched above, inclining downwards or slightly inwards are made in the wood. The resin collects in these in masses or balls, and after a time are collected. Tschirsch examined the system of resiniferous vessels of *Shorea stenoptera*, the product of which he took to agree closely with *Shorea Wiesneri*. There exists in the new wood a system of anastomosed vessels. The resin flow is a result of the wound.

1. *Batavian dammar* was examined by Tschirsch and Glimmann. The sample was completely soluble in chloroform, benzene, carbon disulphide, and sulphuric acid; only partially soluble in alcohol, acetic ether, toluene, acetone, and petroleum ether. It yielded on dry distillation neither benzene nor toluene nor styrol nor phenylacetylene. It was finely pulverized, inserted into the cartridge, and extracted in a Soxhlet's with absolute alcohol. The combined extracts were precipitated by water, which extracts a bitter substance and precipitates the pure resin in flakes. By repeated precipitation the bitter principle is completely removed. The portion soluble in alcohol forms 66 per cent of the resin. It contains no aldehyde. It was dissolved in ether and shaken with 1 per cent potash solution. From the united extracts acidulated by dilute hydrochloric acid a bulky precipitate falls, which on washing shows the property of an apparent acid; dissolved in potash the potassium salt is at once salted out on the addition of potash in sticks, but it cannot be crystallized. However, the acid is obtained as spheritic crystals when the alcoholic solution of the same is precipitated by lead (in the precipitate a small quantity of a second body is found), the lead precipitate filtered from the solution decomposed by sulphuretted hydrogen and the H_2S expelled. The acid was termed dammarolic acid. Analysis (mean of four): C = 76·42; H = 9·24. Calculated for $C_{56}H_{80}O_8$: C = 76·36; H = 9·09 per cent.

The molecular weight was found to be 892; $C_{56}H_{80}O_8$ requires 880. Dammarolic acid dissolves in alcohol, ether, chloroform, benzene, aniline, phenol, sulphuric acid, acetic acid, carbon disulphide; very slightly in petroleum ether. Acetylized, in a tube for twelve hours with acetic anhydride and sodium acetate, dammarolic acid yields an acetyl derivative soluble in petroleum ether which gave the following results. Found mean of four analyses: C = 75·52; H = 8·94. Calculated for $C_{56}H_{79}O_8 . CH_3CO$: C = 75·49; H = 8·89. Benzoylation left a benzoyl derivative which gave the following. Found mean of three analyses: C = 76·61; H = 8·51. Calculated for $C_{56}H_{79}O_8 . C_6H_5CO$: C = 76·83; H = 8·54. Dammarolic acid contains a hydroxyl derivative, $C_{56}H_{79}O_7 . OH$. It does not contain methoxyl. As dammarolic acid in solution reacts acid, the basicity of the acid may be determined by titration with normal alkali and back titration. The titration required 8·5 per cent K to form the K salt; $C_{56}H_{78}K_2O_8$ requires 8·86 per cent K. Dammar-

olic acid is therefore dibasic. The potassium salt was obtained as a dry powder by evaporating the alcoholic solution of the dammarolic acid with potash. It was extracted with absolute alcohol so as to leave all carbonate behind, and the extract evaporated to dryness gave as a mean of four analyses, K = 7·85 per cent. Calculated for $C_{56}H_{78}K_2O_8$, K = 8·15 per cent. The copper salt prepared by precipitating the alcoholic solution by copper chloride gave mean of three analyses, Cu = 6·51. Calculated for $C_{56}H_{78}CuO_8$, Cu = 6·68 per cent. The formula of dammarolic acid can from its behaviour with metals be written as $C_{54}H_{77}O_3 . OH . (COOH)_2$ or as $C_{55}H_{78}O_5 . OH \cdot COOH$. See remarks on formula of trachylolic acid $C_{56}H_{88}O_8$.[1] Strong nitric acid yields picric acid. Along with picric acid a new nitrogen free acid rich in oxygen is produced, preliminarily termed oxydammarolic acid. It gave the following results on analysis: Found: C = 59·78; H = 8·20. Calculated for $C_{40}H_{66}O_{16}$: C = 59·77; H = 8·22. Fused potash does not attack dammarolic acid but very little. The ethereal solution of the resin which has been extracted by caustic potash (in the later phases a stronger solution is required) so as to eliminate completely all the dammarolic acid, leaves behind on the evaporation of the ether a neutral resin, melting-point 65° C., which on boiling for a day (or by steam treatment) with 10 per cent caustic soda cedes nothing thereto and exhibits the properties of a resene. The resene, so boiled, is freed from alkali, dissolved in alcohol, and precipitated with water acidulated by hydrochloric acid. By repeated precipitation a colourless substance is obtained which dissolves in alcohol, ether, and carbon disulphide, etc., melting at 90° C. Analysis (mean of three): C = 80·01; H = 10·25. Calculated for $C_{11}H_{17}O$ or $C_{24}H_{34}O_2$: C = 80·00; H = 10·30 per cent. The substance was termed *a-Dammaro resene*, as the substance is insoluble in potash and indifferent to boiling potash, and it can neither be acetylated nor benzoylated nor saponified, nor does it react with hydroxylamine. *a-Dammaro resene* can, however, be sulphonated. It is not oxidized by permanganate. But concentrated nitric acid acts upon it and gives, when poured into water in which picric acid remains in solution, a nitrogen free oxidation product which gave the following figures. Found: C = 47·04; H = 5·78. Calculated for $C_4H_6O_3$: C = 47·06; H = 5·88 per cent. The residue in the cartridge from the alcoholic extraction of the pure resin on complete extraction with alcohol forms a grey amber-coloured product. It dissolves only in chloroform, and on complete precipitation a colourless powder, melting at 206° C., is obtained. This is evidently the hydrocarbide of the earlier authors. The substance, however, contains oxygen, as the analysis shows. Found: C = 84·52; H = 11·77. Calculated for $C_{31}H_{52}O$: C = 84·55; hydrogen, 11·82 per cent. The substance behaves as a resene; it was termed *β-Dammaro resene*. Dipterocarpus dammar therefore contains:—

[1] This treatise, Vol. II, pp. 51-2.

	Per cent.
Dammarolic acid	23
α-Dammaro resene	40
β-Dammaro resene	22·5
	85·5

2. *Sal dammar* is the product of the *Shorea robusta*, a large tree of 100-130 feet high, all the young parts of which are covered with an ash-coloured down. The petiolated leaves, oval or elliptical, cordate or rounded at the base, are terminated by a short obtuse acumen. Flowers yellowish, with short pedicals, are in axillary or terminal clusters. The sepals are oval, obtusely acuminated, unequal, glabrous within. The petals, four times as long as the limbs of the calyx, are pubescent on the exterior, enlarged at the base, obtuse at the summit. The stamens, 30-40 or more, bearing oval anthers, ciliated at the summit, with recurved connective, ovary trilocular, with two ovules in each dissepiment. Fruit ovoid, pointed, velvety, coriaceous, indehiscent, free in the upper part, and enveloped inferiorly by the swollen unequal lobes of the calyx. This species inhabits Northern India, the Himalayas, Assam, Punjab; it extends into Burma, and possibly as far as Cochin-China. Gamble says this large gregarious tree occupies two principal regions in India: (1) a belt at foot of the Himalayas running into its valleys and up its lower hills, 3000-4000 feet, exceptionally, as at Lansdowne, still higher; (2) the Central Indian belt and the Sal country begins on Ganges, near Rajmahal, passes through Southal, Parganas, Rewah, Chota, Nagpur, Central Provinces, Orissa, Northern Circars, ending in Palkonda range of Vizapatam and the forest of Jeypur. In Telugu, *Guggilam*, in English, Sal dammar tree, the resin known as Bal Dhoona or Sal dammar flows from the trunk in the liquid state and solidifies on the surface. It then occurs as irregular, brittle, cream-coloured or dark brown, almost opaque, striated, stalactitic pieces, as if each stream of resin had coagulated and solidified before the secretion and deposition of the next. Its density is 1·097 to 1·123; it is inodorous and insipid; it melts easily, dissolves partially in alcohol and almost completely in ether; whilst it is perfectly soluble in spirits of turpentine and fixed oils, it is more freely soluble in benzene.

Watt gives the following data: When tapped the tree exudes large quantities of an aromatic resin, whitish at first but becoming brown when dry. The usual method of tapping is, in the month of July, to cut out three to five narrow strips of the bark, according to the size of the tree, and about 3 or 4 feet from the ground. In about twelve days the grooves have filled up with resin. This is gathered and left to fill again. They give three yields, amounting in the best trees to as much as 7 lb. The first is the best in quality. A second yield in October and a third in January are also obtained from the same cuts, but small in quantity and inferior in quality. The resin usually occurs in small, rough pieces, nearly opaque,

but very brittle. Gamble states that in some parts of the Upper Tista forests large blocks, 30 to 40 cubic inches in size, may be found in the ground at the foot of the trees. It is used to caulk boats and ships, also as an incense and in medicine. Hooper says it has a much lower acid value than pine resin, viz. 124 in imported pine resin and 20 to 22 in the Indian article (Watt).

3. *Black dammar* is derived from species of *Canarium*. The *Canarium* are trees growing in India, the Malay Archipelago, and tropical Africa, with alternate imparipinnate leaves and flowers forming clusters of axillary cymes. The corolla comprises three petals slightly coriaceous, much longer than the limbs of the calyx, with valvate or imbricate inflorescence. Of the six stamens comprising the andrecium the three opposite the petals are the shortest. The anthers are introrse; the filaments inserted at the base of a fleshy hypogynous disc are free or more or less adherent to the disc. The ovary is trilocular, the style cylindroid, terminated by a head with three stigmatic lobes. Each dissepiment of the ovary contains two ovules. The fruit is drupaceous, trilocular, but one only of the dissepiments is fertile, with a seed hanging from a membraneous ligument.

3a. *Black Dammar, Kula Dammar, Gugul, Karapu Kongiliam, Karang, Kunthrikam, Kundrikam, Manda Dhup, Raldhup, Thelli.*—These are all native names given to the *Canarium strictum*, a tall tree of Western and Southern India, from the Konkan southwards, and is somewhat common in the Tinevelly and Travancore districts. The trunk is straight, and is, when young, covered with a rust-coloured pubescence (J. Brown). According to Watt, when in young foliage it is almost crimson and is in consequence very conspicuous on the Ghats up to altitudes of 5000 feet (Watt). It grows up to an altitude of 1600 to 2000 feet (J. Brown). The coriaceous leaves consist of three to seven leaflets with short petioles with dentate edges or finely serrate. It yields the resin known as the *black dammar* of Southern India. The native process of extraction is as follows: As the timber is worthless, to obtain the resin the tree is fired in the hot season by making a number of vertical incisions widening out uniformly in the bark in the lower part of the stem. Brushwood is then piled round the base of the tree below the incisions to a height of 3 feet and then set fire to. The heat stimulates the flow of resin from the incisions. In about two years' time the dammar is said to begin to exude from the stem and to continue to flow for ten years afterwards during the months of April to November. The resin as it flows from the incision is allowed to solidify on the spot. The annual yield of a tree is 66 to 68 lb. With the fire-heat method of extraction the tree is killed after ten to twelve years. The collection is made in January and traded in all over South and Western India, but owing to its high price is not much exported. The supply comes chiefly from Travancore and the resin fetches about 3 rupees for 18 lb. It is employed in the manufacture of bottling

wax or for varnish, and in medicine as a substitute for Burgundy pitch in the manufacture of plasters. Black dammar occurs on the tree as shining black lumps, opaque when viewed by reflected light, but in the case of the pieces translucent and deep red by transmitted light. Its structure is homogeneous, its lustre vitreous. Like ordinary dammar it is freely soluble in spirits of turpentine. It is insoluble in cold alcohol, but dissolves in hot alcohol to a certain extent on the addition of camphor. It is soluble in chloroform, very soluble in boiling toluene, which is the best medium to obtain it in the pure state. The solution after filtration is evaporated on the water-bath. The resinous mass in the bottom of the basin is limpid and deep yellow according to the colour of the crude product.

3*b*. *Black Dammar from Canarium Benegalense.*—An allied species, the *C. Benegalense*, Roxb., grows in Sylhet. It is a tree with alternate leaves with sub-opposite leaflets (6-10 pairs), oval, oblong, or lanceolate, acuminate, entire; the subulate stipules are covered with reddish down. The resin is pale amber coloured.

According to Watt, *C. Benegalense*, Roxb., is the *nerebi* of Sibsagar and Sylhet of which Roxburgh wrote: "From fissures or wounds in the bark a large quantity of a very pure clear amber-coloured resin exudes which soon becomes hard and brittle and is not unlike copal, yet the natives set no value on it". "In the Calcutta bazaar it is only valued at 2 to 3 rupees for seven maunds of 80 lb. weight each!" Most writers, concludes Watt, have repeated the above without either correcting or amplifying the information, so that it is not known whether or not the resin is used economically.

3*c*. *Black* (*Assam*) *Dammar.*—Product of *Canarium resiniferum*, Brace (*dhuna dua takreng*, etc.), a large tree of Assam, the Khasia and Garo Hills. This is probably the chief source of the *Canarium* resin of Assam hitherto supposed to be *C. Benegalense*. Gamble says it gives a resin which is used for torches. A small consignment (13 lb.) received by the Indian Government reporter of economic products as fair average quality of black dammar, collected in Cachar, Assam, was reported on by the Imperial Institute. It consisted of large flattened pieces, with small portions of surface-adhering bark. *Colour*—Dull dark brown. *Fracture*—Glassy conchoidal. *Solubility*—Readily in turps, benzene, chloroform, acetic anhydride; partially in alcohol or ether. *Liebermann-Storch reaction*—A drop of concentrated sulphuric acid, added to a solution of the resin, in acetic anhydride, gave a deep purple coloration, which slowly changed to ruby-red. Melting-point, 125° C. Ash, 0·78 per cent. Saponification value, 9·43. Acid value, 8·15. Ester value, 1·28. Results show the resin is of dammar type, yet it differs somewhat from commercial black dammar, stated to come from *C. strictum*, especially in its lower acid and saponification values. Samples were sent to varnish-makers for trial, and with above data to commercial experts for valuation. The former reported the resin as

suitable for hard-drying varnish, for enamels, but that colour would hamper sale, and unlikely that more than 18s. a cwt. would be got for it. Export trade in it from India would depend on whether above prices would be remunerative to Indian exporters and whether supply would be regular.

3*d*. *Canarium Sikkimense* (*Gugal dhup, Nar-ok-pa*).—A very tall tree of Nepal and Sikkim, the inner valleys of the Eastern Hima-

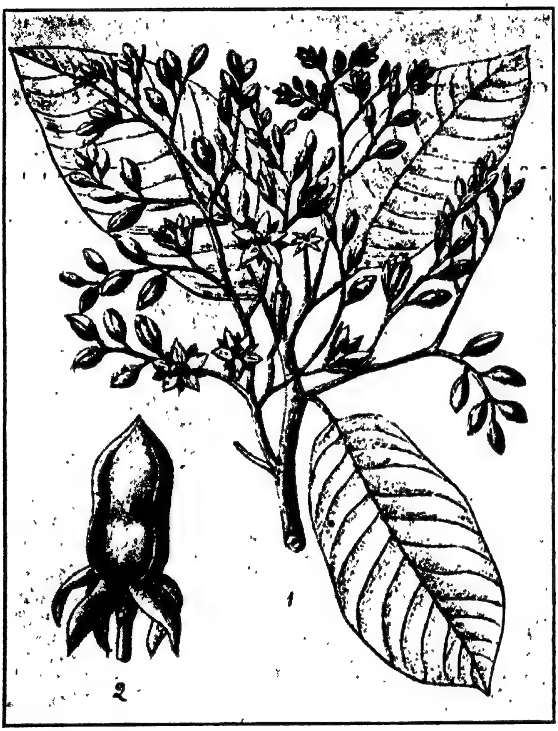


FIG. 27.—*Vateria Indica*. Flowering branch and fruit.

layas, up to altitudes of 3000 feet. Yields a clear amber-coloured brittle resin which is burned as incense by the Lepchas. Dymock speaks of an amber-coloured resin, the incense *gokal dhup*, and he thus doubtless meant this plant and not *C. Benegalense*. *C. Sikkimense* is scarce of late, owing to the demand for tea-boxes. The timber does not warp but decays rapidly.

4. *White* (*Indian*) *Dammar or Piney Resin* (*Gum Piney*).—This true resin of considerable value (Watt) is the product of the *Vateria Indica*, L. (*Vateria Malabarica*, Blume), Nat. Ord. *Dipterocarpeæ*. It

is a large evergreen tree of the forests at the foot of the Western Ghats, from Kanara to Travancore, ascending to 4000 feet. Often planted as an avenue tree. Its young branches and inflorescences are covered with a stillated down. The petiolated leaves are oblong, or elliptical, obtusely or slightly acuminated, rounded or emarginate at the base, and furnished with sharp lanceolated stipules. The inflorescences in loose corymbiform panicles carry pedicellated flowers. The calyx with lanceolated segments is obtuse, pubescent on both sides. The corolla is white with elliptical, oblong, or obtuse petals. The anthers are glabrous. The fruit is an oblong, obtuse, or slightly acuminated coriaceous trivalved capsule.

The native synonyms of the resin are: safed damar, kahruba, sandras, rál, vellai-kunri-kam, painipishin, kungiliyam, piney maram, gugli, dupa maram, dhupada, payani, etc.

Three varieties or forms of this resin are to be distinguished: *compact* piney, *cellular* piney, and *dark-coloured* piney. These names are sufficiently distinctive. But *compact* piney occurs in pieces of various size and shape and gradation of colour, and contains debris of bark. The surface colour shows all gradations from bright orange to dark yellow. It is a very hard resin, with a bright vitreous fracture, recalling amber. In the centre of the pieces the colour varies from pale green to pale yellow, green predominating in most samples. In the *cellular* form the fragments are brilliant and possess a balsamic odour. The resin exudes from incisions made on the tree. The resin is allowed to dry *in situ*, or better, it is dried by fire. It is then pale green or pale transparent yellow. When not perfectly dry the product is dark green, opaque, and full of gaseous air-bells. It is possible, therefore, that the *cellular* structure is due to the action of the fire, which by rapidly volatilizing the essential oil leaves a porous resinous residue. Piney resin exudes spontaneously from the trees, but, in that case, contains many foreign bodies. The most pure product, sold in the Indian bazaars, flows from oblique incisions described above. This resin is slightly soluble in alcohol, but it dissolves in chloroform, spirits of turpentine, and drying oils. The solution in spirits of turpentine is cloudy, but by filtering it through charcoal it becomes bright, colourless, and yields a very pure varnish. According to Cooke, piney resin is not exported and is unknown on the London market. It is only used in India. In the liquid state, before solidification, it constitutes the piney varnish of Malabar. As it burns without smoke, with a bright flame, exhaling a pleasant smell, it is used as an illuminant. It forms, in native industry, the basis of oil and spirit varnish. To prepare an oil varnish 1 part of the pulverized dammar is fused in a closed vessel. When quite fused 2 parts of boiling-hot linseed oil are run on to it and mixed with a wooden spatula. More linseed oil is added if the varnish is too thick. As to the preparation of spirit varnish, as piney resin is not soluble in that vehicle, Wight advises the addition of 1 part of camphor to

6 parts of resin to facilitate solution. But it is advisable before using such a varnish to evaporate the excess of camphor, lest it form a whitish coat on drying.

5. *Rock Dammar* is the product of two species of *Hopea*, the *Hopea odorata* of Rangoon and the *Hopea micrantha* of Sumatra. The resiniferous species of the genus *Hopea* are distributed over India, Burma, Indo-China, and the Malay Archipelago. (1) *Hopea odorata*, Roxb. (*H. Faginea*, Hort; *H. decandra*, Buck; *H. Wightiana*, Miq.; *H. sangal*, Korth; *Doona odorata*, Burch. Burmese: Thungan-tsi, Annamite: Saoden, Kmer: Co Ky), large trees, the young branches and petioles of which are pubescent. Leaves oval or oblong, lanceolate, obtusely acuminate, furnished with twelve pairs of veins, sometimes glandular. The flowers with short pedicels in bunches, shorter or the same length as the leaves. The exterior sepals are velvety on both faces, the interior sepals glabrous within. The stamens bear oval anthers surmounted by a long subulate connective. The fruit is enveloped by portions of the calyx, of which two form oblong linear wings. The species inhabit Burma, Pegu, Rangoon, Martaban, Tenasserim, all equatorial India, Indo-China, and the Isle of Borneo. The *odorata* resin comes to market in straw-coloured hard nodules, about the size of walnuts, with a lustrous resinous fracture and altogether very much like ordinary East India dammar, equal to it in every respect, and even rather superior to it in point of hardness. It is soluble in spirits of turpentine and benzol, yielding a clear, bright, quick-drying uniform varnish. It is insoluble in alcohol. (2) From the trunk and branches of the *Hopea micrantha*, an allied species of the Malay Peninsula, Sumatra, and Borneo, a resin flows in large tears. This resin possibly forms a part of dammar Mata Kuching, said by Cooke to equal Manila and worth £2 the cwt., and scarcely differs from the above, but is rather darker in colour and not so brittle. It is paler in the interior.

A sample of rock dammar was tested by the Imperial Institute for the Indian Government. *Form*—Large irregularly shaped tears. *Colour*—Yellow. *Fracture*—Brilliant irregular. *Odour*—Slight aromatic. Melting-point, 115° C. Saponification value, 37·1. Acid value, 31·5. Ester value, 5·6. *Solubility*—Completely in turps, partially in alcohol. As the different commercial dammars come from diverse plants they vary somewhat in composition and properties, so data from typical varieties cannot be quoted for comparison. Dammars are, as a rule, hard, with brilliant fracture, partially soluble in alcohol and completely so in turps. Their acid values vary—21-34·2 for "Sumatra" to 73 for black dammar. The results of the *H. odorata* resin show it to be a better class dammar. Varnish-makers valued it as second grade, and as fit for crystal or paper varnishes used for indoor work. Value, 45s. per cwt. Demand not great, as varnish not durable enough for outdoor work. But if procurable fossilized the resin would possibly equal

Manila copal, and if the price for fossilized were less, demand would be unlimited.

(3) *Hopea Ferrea*, Pierre. Annamite: Sang da.—A tree of 65 to 100 feet, entirely glabrous with attenuated branches. Leaves petiolated, oval, acuminate, rounded, scarcely oblique, at the base obtuse. Coriaceous with ten pair of small ribs connected by tertiary transversal parallel nervation. The flowers form axillary or terminal clusters longer than the leaves. The fruit is cylindrical, entirely free, with linear calicinary lobes, oblong, rounded at the summit, very attenuated at the base, and furnished with seven parallel veins. This species inhabits lower Cochin-China, also the mountains of Dinh, near to Baria, Camchay, near to Kamphut, and the Isle of Phu Quoe. It yields a very fine and select odorous resin in small yellowish tears.

(4) *Hopea Mengarawan*, Miq.—The tree yielding this resin is known in the Dutch East Indies under the name of Mengarawan. It exudes a white resin highly esteemed for the brilliant varnish made from it. It is a large tree abundant in the low-lying districts of Palembang, Lampong, and Bangka. (See No. 8, pp. 208-9.)

TABLE LVI.—RESINIFEROUS *SHOREA* OF FRENCH COCHIN-CHINA.

Botanical Designation.	Native Designation.	Habitat.	Remarks.
Shorea Hypochra, Hance.	Annamite:— *Vin Vin Nghe. Vin Vin Xanh.*	Isle of Phu Quoe and the province of Kamphut.	Yields an abundant flow of amber-coloured resin, which is exported.
Shorea Cambodia, Pierre.	Kmer:— *Dom chhoeu phdiec crohom.*	Mountains and coast of Kamphut and chiefly the base of Talung.	Amber-coloured somewhat odorous resin esteemed for exportation.
Shorea Thorelli, Pierre.	Annamite:— *Sen Chochai.* Kmer:— *K'tiaou or K'tim.*	All the provinces of Cambodia and lower Cochin-China, chiefly the mountains of Pusath Camchay and the forests near the rivers of Saigon and Dong-nai.	Yields a large quantity of excellent resin.
Shorea Obtusa, Wall. *S. leucobotrya*, Miq. *Vatica Obtusa*, Steud.	Annamite:— *Kachac.* Kmer:— *Dom chhoeu Phehoc.*	Grows throughout all Indo-China from Burma to Binh-tuan. It is common in Cambodia on gravel soils and on all the mountains and in lower Cochin-China from the left bank of the Mekong as far as Songbe.	The very abundant white resin is used in making torches and is exported into China.

Chai Pitch.—All the above species of *Shorea* are used in making the native chai-pitch. This resin is in fact called Chai in Annamite and Tior Tiong in Cambodian. It is doubtless chiefly obtained from *S. Thorelli* and *S. obtusa* which are the most widely distributed species (Pierre). It is collected abundantly in the district of Tay-ninh. Chai pitch is insoluble in alcohol, ether, spirits of turpentine, and benzene, but it is soluble in toluene and dissolves completely in chloroform. To get the pure resin chloroform is therefore the best solvent. The solution is filtered and evaporated. The residue on the filter is almost nil. After evaporation on the water-bath it remains on the bottom of the dish as a slightly reddish pale yellow resin which dries slowly. The following are further particulars in regard to this resin: It exudes naturally from the tree after the fine punctures made by insects. It solidifies in large tears or flows to the foot of the tree, where the natives have only got the trouble to come and collect it when it is dry. It is brittle, splintery, and has some analogy with pine resin. After pulverization wood oil (daû con rai) is added to it, and oakum and the mixture kneaded so as to give it suppleness and the desired consistency. In this way the Annamites and the Chinese use chai resin for caulking ships and junks. They also use it for torches and flambeaux. A brisk trade is done in this resin, which is sold at the rate of 3 piastres the picul of 60 kilogrammes. The trading ships of the Tayninh district annually export a large quantity. This product is so esteemed that the Chinese of Cholon and Western districts come to supply their wants on the spot of production. Sometimes it affords a means of speculation on the part of the Annamite merchants of the town, who corner all the production and sell it at a high price to the Chinese buyers. This is a resin of which a plentiful supply could be got if the method of working were more methodical and if the natives pushed their efforts further than the mere collection of the spontaneously exuded resin. Moreover, it is a really valuable substance, which might be the medium of much more extensive commercial transactions and find its use in European industry.

Nine samples of dammar resin from the Federated Malay States have been examined. These were as follows: (1) Dammar Penak, No. 1 quality, from *Balanocarpus* (*Maximus* or *Wrayi*); (2) Dammar Kumus from a species of *Shorea*, probably *S. glauca;* (3) Dammar Mata Kuching from Port Dickson; (4) Dammar Soongyi; (5) Dammar Meranti, a mixed material obtained from various species of *Shorea;* (6) Dammar Mata Kuching from Jempol; (7) Dammar Rengkong (?); (8) Dammar Merawan; (9) Dammar Strayah.

These dammars were all completely soluble in turpentine, and partially soluble in alcohol. The figures obtained on analysis varied somewhat, and were as follows:—

TABLE LVII.—SHOWING THE CHEMICAL AND PHYSICAL PROPERTIES (CONSTANTS) OF NINE DIFFERENT VARIETIES OF DAMMAR.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Melting-point	90° C.	94° C.	87° C.	180° C.	185° C.
Ash per cent	0·26	0·08	0·05	0·52	0·03
Sap. number	46·7	72·0	38·5	34·3	72·0
Acid ,,	45·3	72·0	38·5	33·0	72·0
Ester ,,	1·4	—	—	1·3	—

	No. 6.	No. 7.	No. 8.	No. 9.
Melting-point	92° C.	200° C.	97° C.	190° C.
Ash per cent	0·06	0·04	0·25	0·09
Sap. number	33·0	46·7	38·5	55·0
Acid ,,	33·0	46·5	38·5	55·0
Ester ,,	—	0·2	—	—

From the above descriptions of the different varieties of dammar it will be readily seen that dammar is a generic term, not a specific one. Stewart in his method of detecting dammar in kauri has forgotten this point. He has tried to show that when absolute alcohol is added to an ethereal or chloroform solution of dammar, a white precipitate is formed, while a solution of kauri remains quite clear just as if there was only one kauri and one dammar, and the solubility of both dammar and kauri was like the law of the Medes and Persians which altereth not. This he used as a rough quantitative test: 0·5 gramme of the powdered resin is treated with chloroform and filtered into a test tube, washing the residue once; to the solution absolute alcohol is added, which produces, he asserts, a white cloudiness or precipitate if dammar is present. By comparing the result with mixtures of known composition a fair approximation to the amount of dammar can, he claims, be obtained.

Quantitative method: 2½ grammes of the sample are weighed in a tared ribbed filter. The filter is then tied at the open end and extracted in a Soxhlet tube with absolute alcohol. The remainder of the Soxhlet tube is filled with small glass balls to allow of the minimum quantity of solvent being used. The solution may be collected in a weighed flask, and the alcohol distilled off; but as there is a loss of volatile matter from the resin during drying, it is better to dry and weigh the residue on the filter, the difference being the soluble resin. With a pure kauri resin the amount of residue left on the filter paper is very small, and consists of fragments of vegetable and mineral matter. With dammar resin, in addition to vegetable and mineral matter, there is a considerable proportion of white organic particles insoluble in the alcohol. The amount of this substance is estimated by extracting again in the

Soxhlet tube, using chloroform as the solvent, and the extract being collected in a weighed flask, the solvent is distilled off, a little alcohol is added to facilitate evaporation and the residue is dried at 100° C. and weighed.

As the amount of insoluble matter in dammar may be variable in the case of adulterated samples, portions supposed to be dammar were picked out, tested with chloroform and alcohol to verify them, and when enough had been obtained they were examined in the same way as the suspected sample. The following results are given in the paper :—

TABLE LVIII.—SHOWING SOLUBILITY OF KAURI AND DAMMAR IN ABSOLUTE ALCOHOL AND IN CHLOROFORM.

	Soluble in Absolute Alcohol.	Insoluble in Absolute Alcohol, Soluble in Chloroform.	Vegetable Matter Non-Resinous.	Mineral Matter.	Percentage of Dammar Calculated.
1. Kauri	91·56	none	3·28	5·16	—
2. Dammar	58·28	36·40	3·24	2·08	—
3. { Kauri (1) 80 per cent Dammar (2) 20 per cent }	85·82	7·30	2·38	4·50	20·05
4. Sample K	81·16	13·88	1·48	3·48	28·16
5. Dammar from 4	50·22	49·28	0·38	0·12	—
6. Sample G_1	81·72	9·72	2·70	5·86	20·23
7. Dammar from 6	50·95	48·05	0·70	0·30	—
8. Sample G_2	81·00	10·80	2·84	5·36	21·60
9. " G_3	81·72	8·80	2·68	6·80	17·60
10. " F_1	82·20	4·52	3·68	9·60	9·04
11. " F_2	85·08	4·80	4·48	5·64	9·60
12. " grains	81·04	0·48	9·28	9·20	0·96
13. " G_4	89·84	1·60	3·12	5·44	3·20
14. " F_3	86·00	7·84	2·68	3·48	20·33
15. Dammar from 14	61·24	38·56	0·08	0·12	—

The quantities of dammar in Nos. 8, 9, 10, 11, 12, and 13, were calculated on the assumption that dammar yields 50 per cent of the white insoluble matter. Stewart's logic is faulty. He seems to reason thus: One sample of kauri gave certain results, *ergo* all samples of kauri will give identical results, and the same as regards dammar. It is very evident from the ash that Stewart wrought not upon sophisticated kauri, but on say sandy sweepings from a gum warehouse or the hold of a ship, where different resins and different grades of the same resin had got intermingled and the mixtures were so poor that they were not worth garbling.

TABLE LIX.—SOLUBILITY OF DIFFERENT GRADES OF KAURI IN CHLOROFORM AND ALCOHOL (PARRY).

	White Kauri.		Brown Kauri.		Pale "Bush" Kauri.		Dark "Bush" Kauri.	
	Soluble in Absolute Alcohol. Per cent.	Soluble in Chloroform. Per cent.	Soluble in Absolute Alcohol. Per cent.	Soluble in Chloroform. Per cent.	Soluble in Absolute Alcohol. Per cent.	Soluble in Chloroform. Per cent.	Soluble in Absolute Alcohol. Per cent.	Soluble in Chloroform. Per cent.
(1)	92·6	45·0	68·5	40·0	95·2	50·0	84·0	45·0
(2)	93·5	44·4	74·2	42·3	93·1	49·9	83·7	44·6
(3)	91·0	40·8	66·3	39·2	92·0	53·4	79·5	41·9
(4)	94·3	43·5	67·5	38·7	93·2	47·7	82·5	43·5
(5)	92·0	44·0	68·2	40·0	—	—	—	—
(6)	89·9	47·2	61·9	39·6	—	—	—	—

N.B.—Compare above positive (solubility) figures with Coffignier's negative insolubility ones.

But both Stewart and Parry overlook the fact that most, if not all, dammars are soluble in turps whilst all grades of kauri leave a residue of about 25 per cent. Surely the most simple plan would be, therefore, to take the insoluble in turps as the basis in which to calculate the amount of dammar present, that is, if solubility lent itself at all to such determinations. It seems so difficult for some to realize that the solubility of a resin in any given solvent is *not* as definite and absolutely fixed a factor as the solubility of pure crystallized cane sugar in water.

CHAPTER XVI.

DRAGON'S BLOOD, ELEMI, GAMBOGE, GURJUN BALSAM, JAVA COPAL, GRASS-TREE "GUM".

Dragon's Blood.—A large number of substances, quite different from one another in composition and properties, and which have no common properties except their red colour, have been erroneously classified as dragon's blood. In fact, some tanno-gums and kinos have been regarded as dragon's blood. The true dragon's blood is the product of the *Calamus draco*, Wild (*Dæmonorops draco*, Blume), a Malay palm allied to the rattan with a stem bristling with sharp spines. This climbing stem may rise to a considerable height. It is not cultivated, and only the trees growing wild in the forest are exploited. The resin exudes from the fruits. The *C. draco* bears a great number of rounded fruits of the size of a cherry, the surface of which is covered with smooth imbricated scales. The latter on maturity are enveloped in a layer of friable red resin. The fruits are then collected, beaten in sacks to detach the resin, which is sifted to separate the fallen scales. It is beaten in boiling water and kneaded into balls (dragon's blood olives) or in long thin cylinders (dragon's blood in sticks). These are the most esteemed. The fruits which have been used in the preceding operation are crushed and boiled in water; the resin which they contain floats to the top. It is separated and made into cakes (dragon's blood in cakes). The ligneous residue which has been boiled is kneaded into balls and sold as common or lump dragon's blood. Contrary to what one might believe, it still contains a comparatively high proportion of resin. Good dragon's blood is dark red, opaque, and friable. Its fracture is red and brilliant. Its odour and taste are scarcely appreciable. Its powder is red vermilion and slightly soils paper. Insoluble in water, it is almost completely soluble in alcohol, benzene, chloroform, carbon disulphide. The residue left on the filter consists solely of woody impurities, always present in the crude product. The natural resin of *C. draco* contains benzoic acid. Herberg described its composition in the "Journal de Pharmacie," XVII, 1831, p. 225.

Amorphous resin and acid	90·70
Fatty matter soluble in ether	1·60
Phosphate and oxalate of lime	3·70
Benzoic acid	3·00

Several *Dracæna* secrete from their trunk a brown-red resin which is not utilized. The *Dracæna* are arborescent, liliaceæ, widely distributed in hot countries and in the South of Europe. Some species furnish a notable amount of this reddish juice, which concretes in the open air, e.g. *D. draco* and *D. Australis*. The last species was examined by Cordemoy. It is dark brown, irregular pieces, friable, with a somewhat shining fracture. Its powder is reddish-brown. It only dissolves partially in absolute alcohol and in ether, but its solubility in ether is greater than in alcohol. The alcoholic solution is bright red, the ethereal solution is dark red. The filtered liquors evaporated on the water-bath leave a pasty substance at the bottom of the dish, black, seen in the mass and which solidifies rapidly. But in a thin layer this resin so purified furnishes a brilliant mahogany varnish. Logander gives the following information regarding different varieties of dragon's blood: (1) Soluble in benzol and carbon disulphide. Dragon's blood of *Dæmonorops draco*, $C_{18}H_{18}O_4$. Melting-point, 80°-120° C. Contains pure resin 82 per cent; benzoic acid 3 per cent; cinnamic acid, mineral matter 6 per cent. *Dry Distillation Products.*—Toluene, styrol, benzoic acid. *Oxidation Product with* KOH.—Phloroglucin, *p*-oxybenzoic acid, protocatechuic acid, benzoic acid, acetic acid, acetone, oxalic acid. *Reduction by Zinc Dust.*—Toluene, styrol, ethyl benzol, $C_{11}H_{10}O$, $C_{13}H_2O_7$, $C_{16}H_{20}O_3$. (2) Insoluble in benzene and carbon disulphide. Dragon's blood of *Dracæna cinnabri*, $C_{18}H_{18}O_4$. Melting-point, 80. Contains pure resin 85·35 per cent; gum 0·7 per cent; carbon disulphide extract 0·48; plant debris 12 per cent; mineral matter 3·5 per cent. *Products of Dry Distillation.*—Cresol, guaiacol, pyrocatechin. *Products of Oxidation with* KOH.—Resorcin, phloroglucin, pyrocatechin, benzoic acid, acetic acid. *Oxidation with Caustic Soda.*—Pyrocatechin and phloroglucin. *Treatment with* HNO_3.—Picric acid, nitro-benzoic acid. (3) Dragon's blood from *Dracæna draco*, $C_{18}H_{18}O_4$. Melting-point, 60° C. (4) Dragon's blood from *Dracæna Schizantha*. Melting-point, 70° C.

Palm Dragon's Blood. Method of Analysis.—The dragon's blood is dissolved in ether which leaves 18·4 per cent of plant residue; a brown body 0·33 per cent is extracted from the plant residue by alcohol. By running the ethereal solution into alcohol, 2·5 per cent of a substance, draco alban, is thrown out. By evaporating the ether alcohol and extracting the solid residue with petroleum ether, a rosin-like mass is obtained forming 13·58 per cent of the resin with the properties of a resene, draco resene. There remains from this treatment a reddish-coloured body with the composition of a resin or resin ester, viz. draco resin, 58·86.

TABLE LX.—COMPOSITION OF PALM DRAGON'S BLOOD.

	Per cent.
Draco alban $C_{20}H_{40}O_4$	2·5
Draco resene $C_{20}H_{44}O_2$	13·58
Draco resinotannol benzoate $C_6H_5COOC_8H_9O$ Draco resinotannol benzoylacetate $C_6H_5COCH_2COOC_8H_9O$ B-Draco resinotannol monacrylate	56·89
Phlobaphene	0·03
Vegetable residue	18·40
Ash	8·3

Elemi Resins.—The name "elemi resin" is applied to the

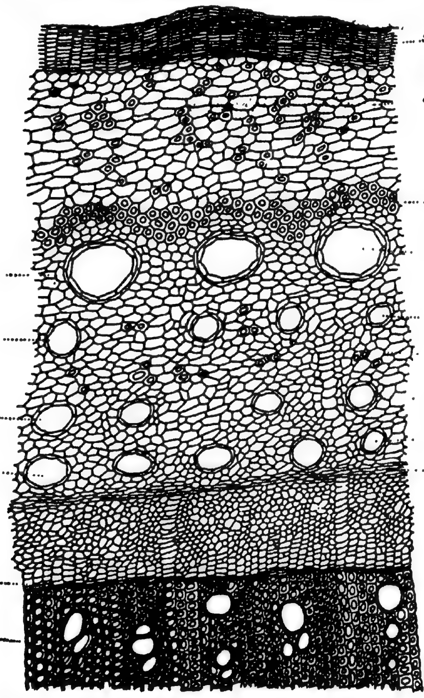


FIG. 28.—*Dacroydes Hexandra griseb Bursera Acuminata Willd, Pistacia Occidentalis* HBn. One of the sources of resina gommert. *s*, cork; *d*, fibrous cells isolated or in small groups throughout the bark; *ec*, bark; *f*, pericyclic fibres in a continuous layer protecting exteriorly the premier secreting vessels of the liber; *cs*, secreting vessels developed in the liberian layer *p* and forming four concentric rows. The row nearest the outside consisting of the widest vessels belongs to the primary liber, all the others to the secondary liber; *l*, the newly formed secondary liber, where no differentiated secreting vessel is to be observed; *n*, the layer of flattened liberian elements; *b*, wood; *b*, libero ligneous generating layer.

resins of the *Amyrideæ* (*Burseraceæ*), all of them products more or less rich in ethereal oils. According to their consistency they are divided into balsams and resins, the former greenish, the latter

yellow to white in colour; initially, they resemble turpentine, but gradually part with their ethereal oil and become solid.

FIG. 29.—*Protium Guianense*, L. March. 1, branch and inflorescence after nature, 2, 3, 4, after Engler; 2, flower; 3, longitudinal section; 4, fruit.

The following furnish elemi resins: *Icica icicariba*, DC., in Brazil (Rio elemi); *Amyris Plumerii*, DC., in Yucatan and Mexico; *Icica viridiflora*, in Guyana (Guiana elemi); certain species of *Burseraceæ*, not clearly defined, in Gaboon (Eoume elemi); *Bursera*

gummifera, L., in Martinique and Guadeloupe (Gommart resin); *Canarium commune*, L., throughout the entire Indian peninsula and Malabar (Junglee-baddam resin); *Ailanthus Malabarica*, DC., in Travancore and Malabar (Mutti-pal resin); *Cassia auriculata*, L., throughout India (the resin is known as Thengatee, Tanggayree, Turwer, and Averie resin). Similar resins are known in India as Kunnee, dammar Keye, Gutta Burghas, and Mal Shaksi, but the plants from whence they are derived have not been identified. Solid elemis are rich in crystallizable matters, only small quantities of which occur in the balsams, the proportion increasing as the solidification of the *Burseraceæ* resins progresses. Even when present in considerable amount, the microscope fails to detect crystalline bodies, because the crystals and surrounding matrix exhibit the same coefficient of refraction, so no optical differentiation is possible. But by treating a sample of elemi resin with alcohol on a microscope slide, the amorphous matrix is dissolved and leaves behind a multitude of acicular or prismatic crystals. The crystals of elemi resin can be detected without any preliminary treatment by the polariscope. All solid elemis are very soft, being inferior in hardness to ordinary rosin, and can be shaved with a knife, like soap-stone, a peculiarity they share with no other resin. The odour is always similar to turpentine, and recalls aniseed, caraway, fennel, or dill seed, according to the kind of resin. The taste is aromatic, bitter, and somewhat carminative. The specific gravity of elemi is 1·018 Brisson, 1·083 Pfiff. These differences are not entirely due to variations in the kind of resin, but also to differences in the degree of solidification. Schroeder gives the softening temperature of elemi as 0° C., and the melting-point as 120° C. The amorphous portion is soluble in cold alcohol, the crystallizable being dissolved only in boiling alcohol. Johnstone gives the formula of the amorphous as $C_{40}H_{64}O_4$, and Rose that of the crystalline as $C_{40}H_{66}O$. All the elemi resins also contain a larger or smaller proportion of an oil isomeric with turpentine oil ($C_{10}H_{16}$), the quantity ranging from 3·5 per cent (Stenhouse) to 13 per cent (Deville), according to the degree of solidification. The above data show that the external and internal properties of elemi resins agree pretty closely, even in very different varieties. Whether the chemical behaviour similarly agrees has not been determined. From analysis of Cayenne elemi and Manila elemi by Scribe and Baup, the chemical bodies found therein (e.g. breane, icicane, breine, etc.) do not agree with those discovered by Johnstone and Rose.

Some commercial varieties come from South America, others from Africa and India, only the two first, however, being important, as so-called Indian elemi does not come from the East Indies.

Manila Elemi is a product of a *Canarium* indigenous to the Philippine Isles, especially Luzon, known under the name of the bread tree, *Canarium luzonicum*. It is met with in soft mass of a granular structure containing disseminated crystals. The colour

varies from greenish-white to yellow. It often contains impurities. Its odour is pleasant, recalling that of fennel or of essence of lemon and turpentine. It is exported to this country from Manila. It is only slightly soluble in cold alcohol though dissolving readily when melted, subsequently depositing crystals.

A. M. Clover has examined Manila elemi from *Canarium luzonicum*. Twenty-one samples were separately examined. On distilling under 10 to 15 mm. ten of the samples yielded pure d-limonene, and nine varying quantities of phellandrene. Pinene was not identified in any sample, but l-limonene, and probably another similar terpene, were present in some. Two samples yielded terpenes with no rotation, which were found to be terpinene and terpinolene. When freshly distilled the terpinolene is practically pure, but on standing or when heated it gradually changes into dipentene, a small quantity of d-phellandrene, and an unknown levo-rotatory terpene.

It is only slightly soluble in cold alcohol, though dissolving readily when melted, and subsequently depositing crystals. This resin is about five times as dear as it was a few years ago, and consequently its employment is restricted. It is used in medicine as an ingredient of salves and plasters, to impart elasticity to spirit varnishes, and for the same purpose in hat-making; also in the preparation of bronze tinctures. Spirit varnishes prepared with elemi have the advantage over those containing turpentine that they are less liable to crack owing to the fact that elemi requires a much longer time to set thoroughly hard.

Elemi from *Canarium luzonicum* (*Canarium commune* [?]).—Quite liquid when fresh with from 25 to 30 per cent of volatile oil, composed of hydrocarbons chiefly of phellandrene. On standing it gradually solidifies to a soft resinous product. The non-volatile portion consists principally of *a* and *β* amyrin. Oleo-resins resembling elemi have occasionally been received from Liberia, Kamerun, Southern Nigeria, and other places on the West Coast of Africa, but the botanical sources are not known. Two samples of Nigerian elemi received from Alexander Brothers of Liverpool, were examined at the laboratories of the Imperial Institute. No. 1 sample was white or pale yellow, with patches of brown; contained much vegetable debris and was sufficiently hard to retain its shape when cut. No. 2 sample was yellowish-green, of firm consistency, and contained a little woody tissue. A sample of Uganda elemi from *Canarium Schweinfurthi* was also examined. This varied in colour from white to pale yellow, but was dirty looking and contained much woody fibre.

TABLE LXI.—CONSTANTS OF AFRICAN ELEMI.

	Nigerian Elemi. 1.	Nigerian Elemi. 2.	Uganda Elemi.	
Ash	0·6	0·58	0·3	
Acid number	55·3	37·8	29·4	On picked clean portion
Saponification number	71·9	46·2	44·8	On picked clean portion
Volatile oil, per cent	8·1	4·4	11·2	

These oleo-resins were practically entirely dissolved by benzene, turpentine, and alcohol, but only sparingly by cold alcohol. The volatile oils separated by steam distillation had the following relative characteristics:—

	Manila Elemi.	W. African Elemi.	Uganda Elemi.
Colour.	Colourless or Pale Yellow.	Pale Straw-Yellow.	Pale Straw-Yellow.
Specific gravity at 15° C . .	0·87-0·91	0·8686	0·8451
Rotation in 100 mm. tube .	+ 44° 3	+ 50° 30	+ 79° 20

Elemi is used in printing-ink manufacture and occasionally in varnishes, but there is no great demand for it, the supply from the Philippines being quite sufficient for all purposes. The price is from 50s. to 70s. per cwt.

TABLE LXII.—SOLUBILITY OF DIFFERENT BRANDS OF ELEMI IN VARIOUS SOLVENTS (DIETERICH).

	Soft Manila Elemi.	Hard Manila Elemi.	Yucatan Elemi.	Vera Cruz Elemi.	African Elemi.	Protium Allmessega Elemi.
Water . . .	i.	i.	i.	i.	i.	i.
Alcohol, 96 per cent .	a.t.c.s.	a.c.s.	a.c.s.	p.t.a.c.s.	a.c.s.	a.t.c.s.
Ether . . .	c.s.	p.s.	a.c.s.	c.s.	a.c.s.	c.s.
Acetic ether . .	a.t.c.s.	a.t.c.s.	c.s.	p.t.a.c.s.	sl.t.a.c.s.	p.t.a.c.s.
Petroleum ether .	sp.s.	sp.s.	sl.s.	i.t.v.sl.s.	sl.s.	s.tl.p.s.
Turps . . .	p.t.a.c.s.	p.s.	a.c.s.	sl.t.p.s.	a.c.s.	p.s.
Benzine . . .	p.t.a.c.s.	p.s.	sl.t.a.c.s.	i.t.v.sl.s.	sl.s.	v.sl.s.
Benzol . . .	c.s.	a.c.s.	c.s.	a.c.s.	a.c.s.	a.c.s.
Carbon disulphide .	c.s.	p.t.a.c.s.	c.s.	a.c.s.	p.t.a.c.s.	a.c.s.
Chloroform . .	c.s.	a.c.s.	c.s.	a.c.s.	a.c.s.	c.s.
Acetone . . .	p.t.c.s.	p.s.	c.s.	p.t.a.c.s.	sl.t.p.s.	p.t.c.s.
Methyl alcohol . .	sp.t.c.s.	a.c.s.	p.t.c.s.	sp.s.	sl.t.p.s.	p.s.
Amyl " . .	c.s.	p.t.a.c.s.	a.c.s.	a.c.s.	—	—
Acetic anhydride .	v.sl.s.	p.s.	p.t.c.s.	sl.t.p.s.	p.t.a.c.s.	p.t.a.c.s.
Methycal . . .	v.sl.s.	p.s.	a.c.s.	sl.t.p.s.	p.t.a.c.s.	sl.t.p.s.
Chloral hydrate, 60 per cent . .	sp.s.	p.s.	im.s.	sl.t.p.s.	sl.s.	p.s.
Chloral hydrate, 80 per cent . .	p.t.c.s.	p.s.	im.s.	p.s.	p.s.	m.s.
Acetic acid . .	p.t.c.s.	sp.s.	p.s.	p.s.	sl.s.	p.t.a.c.s.
Hydrochloric acid .	s.s.(rose)	i.	a.i.	a.i.	p.s.	a.i.
Sulphuric acid . .	a.c.s. red brown	a.c.s. red brown	c.s. dark red	a.c.s.	a.c.s.	a.c.s.
Ammonia . . .	i.	sl.s.	i.	sl.s.	sl.s.	sl.s.
Caustic potash . .	i.	sl.s.	i.	sl.s.	sl.s.	sl.s.

a.	almost.	sp.s.	sparingly soluble.
c.	completely.	p.t.a.c.s.	partly to almost completely soluble.
i.	insoluble.	c.s.	completely soluble.
m.	mostly.	p.t.c.s.	partly to completely soluble.
p.	partly.	sp.t.c.s.	sparingly to completely soluble.
s.	soluble.	v.sl.s.	very slightly soluble.
sl.	slightly.	a.c.s.	almost completely soluble.
sp.	sparingly.	p.s.	partly soluble.
t.	to.	sl.s.	slightly soluble.
v.	very.	im.s.	imperfectly soluble.
a.t.c.s.	almost to completely soluble.	sl.t.a.c.s.	slightly to almost completely soluble.
c.s.	completely soluble.	m.s.	mostly soluble.

TABLE LXIII.—CONSTANTS OF ELEMI (DIETERICH).

	Soft Manila Elemi.					Hard Manila Elemi.
	1	2	3	4	5	6
Loss at 100° C., per cent	16·64	11·71	15·14	19·29	8·46	17·71
Ash, per cent	0·052	0·14	0·10	0·03	0·93	0·14
Acid value *d*	18·03-17·7	17·87-17·97	19·05-19·46	18·68-18·73	18·02-18·07	17·87-17·97
Ester value	7·64-9·91	8·11-7·72	6·15-6·03	6·70-7·71	26·99-24·40	8·11-7·72
Saponification value *h*	25·72-27·68	25·92-25·69	25·20-25·49	25·38-26·44	45·01-42·47	25·92-25·69

	Hard Manila Elemi.		Yucatan Elemi, Soft.	Yucatan Elemi, Hard.	Vera Cruz Elemi.	Vera Cruz Elemi.
	7	8	9	10	11	12
Loss at 100° C., per cent	6·74	10·25	17·07	17·86	5·02	4·90
Ash, per cent	3·43	0·06	0·03	0·39	0·24	0·06
Acid value *d*	21·84	5·71-4·49	22·50-22·29	1·16-1·70	5·98-5·64-11·72	36·47-34·85-36·79
Ester value	45·80-45·72	34·96-27·05	5·68-9·81	35·42-36·36	40·29-28·34-37·32	49·78-38·15-42·10
Saponification value *h*	67·64-70·05	40·67-31·54	28·18-32·10	36·58-38·06	46·27-33·98-49·04	86·25-73·00-78·89

	African Elemi, Luban Matti.			Indian Elemi.	Protium.	Resina Gommert.
	13	14	15	16	17	18
Loss at 100° C., per cent	6·06	1·86	5·89	3·38	2·87-1·66	1·69
Ash, per cent	3·52	0·63	1·19	0·16	0·32-0·44	0·14- 0·15
Acid value *d*	13·29-14·23	14·59-15·09	35·80-37·33	32·46-35·77	38·45-39·41	46·41-47·42
Ester value	47·87-45·18	15·74-15·56	54·14-55·71	54·48-64·04	35·82-34·23	53·76-51·92
Saponification value *h*	61·16-59·41	30·33-30·65	89·94-93·04	86·94-100·17	74·27-73·64	100·17-99·34

Gamboge, Fr. Gomme Gutte.—This yellow gum resin is produced by several species of guttiferæ of the genus *Garcinia*, a genus comprising numerous species of tropical evergreen trees. This species are Asiatic, being more particularly native to Indo-China, Siam, India, Ceylon. In the British Indies none of the species extend to Punjab, or the United Provinces, and few even to the N.E. Himalayas. Most of the thirty-six species contain a yellow juice which mostly yield, in the various grades of gamboge produced therefrom, a more or less useful water-colour pigment. They are trees with opposite leaves, rarely verticillate in threes. The diaceous flowers spring from the axis of the leaves; they are fasciculated; the female flowers often solitary. The sepals most frequently are unequal, longer, shorter, or the same length as the petals. The andrœcium is characterized by anthers more or less exactly confluent top and bottom, consequently forming an annular loculus. These loculi are partitioned transversely into dissepiments. The dehisence of these anthers is similar to that of the pyxides (many-seeded fruits), the upper part of which falls off like a lid by circumscissile dehisence as in piniperene and henbane. The ovary most frequently has four dissepiments, and the stigma has four lobes arranged like the branches of a maltese cross.

The *Garcinia*, with which we are concerned, have two floral characteristics in common. The receptacle is more or less convex and the filamentous stamens are very short.

Indian gamboge is the gum resin secreted by the *Garcinia Morella*, an evergreen tree of the forests of the Khasia hills, Eastern Bengal, the West Coast, and Ceylon. The gamboge of European commerce comes from Siam and is obtained from *Garcinia Hanburyii* (Hook). This tree grows not only in Siam but in Cambodia and in all Indo-China. In Siamese it is *Roeng;* in Annamite *Vangnhua;* in Kmer *Dom rond;* in Chinese *Hoam-lo.* Gamboge has been known from ancient times. Clusius was the first European writer to mention it, in 1605. But Chinese books refer to it in the thirteenth century. The gum resin is not collected to any extent in India, that country receiving its main supply from Siam. The trees are ten years old before spiral tapping, which is done during the rainy season (June to October), when sap is vigorous. The spiral is cut round the trunk 10 feet from base. The resin trickles down into hollow bamboos at the foot of the tree. From these it is decanted into smaller bamboos and left a month or so to solidify. The bamboo joints placed over a hot fire crack and a round stick of gamboge is obtained from each, the roll or pipe gamboge of commerce. This method is not, it seems, used in India, where only small cuts are made and the resin collected in tears. In Ceylon cake and granular gamboge are obtained by cutting here and there a thin slice off the bark and scraping off the resins which collect, but both are less pure than Siam pipe. The best samples of pipe gamboge are of a rich orange-yellow colour, slightly inclined

to fawn; it becomes a brilliant pale yellow when rubbed with the moistened finger. It is dense and brittle like glass. Its fracture

FIG. 30.—*Garcinia Morella.*

FIG. 31.—Pipe Gamboge.

[Photo taken by Mr. Chas. Harrison of the Borough Polytechnic specially for this treatise.]

is conchoidal, smooth, and shining, and of a reddish-yellow colour, which soon changes to liver colour, the surface becoming coated with a dark green layer. It is inodorous. Its taste is slight at

first, but it produces an after-taste in the back part of the palate or throat which is unpleasantly acrid. The streak is lemon-yellow changing to orange. Its powder is a brilliant yellow, but it is less dark than the surface of the section. Mixed with water gamboge forms a beautiful yellow emulsion which is used in water-colour painting. It dissolves completely when treated successively with alcohol and ether. When it is pure a decoction of its fresh powder is fawn coloured. Low grades give a brownish or blackish-green and do not dissolve completely in water and ether applied in succession. A decoction of their powder is coloured green by tincture of iodine, a reaction which shows the presence of starch (the starch coloured blue by the iodine forming green with the yellow of the gamboge). Now starch is not present in good samples.

Composition.—Gamboge contains, according to the kind, 35 to 80 per cent of yellow resin and 14 to 19 per cent of gum soluble in water. The following proximate analyses of different varieties of gamboge are by Castelloe :—

TABLE LXIV.—CASTELLOE'S ANALYSES OF GAMBOGE.

	Lump. Per cent.	Pipe. Per cent.	Powder. Per cent.
Resin	67·6	79·30	76·6
Gum	27·4	19·45	22·5
Impurities	3·8	0·15	0·7
	98·8	98·90	99·8

and these by Sir Robert Christison :—

TABLE LXV.—CHRISTISON'S ANALYSES OF GAMBOGE.

	Pipe Gamboge. Cake Gamboge. From Siam.				Gamboge. From Ceylon.			
Resin	74·2	71·6	64·3	65·0	68·8	71·5	72·9	75·5
Gum	21·8	24·0	20·7	19·7	20·7	18·8	19·4	18·4
Amylaceous (starchy) matter	—	—	6·2	5·0	—	—	—	—
Woody fibre	—	—	4·4	6·2	6·8	5·7	4·3	0·6
Moisture	4·8	4·8	4·0	4·6	4·6	—	—	—
	100·8	100·4	99·6	100·5	100·9	96·0	96·6	99·3

Recently D. Hooper has examined a sample of gamboge from another species of *Garcinia*, *G. cowa*, from Chittagong, and finds that it contains a higher percentage of resin than the ordinary variety. The sample analysed gave the following figures on analysis: Resin 84·3, gum 5·6, mineral matter 1·1, moisture 6·5, residue 2·5 per cent. This gum resin is paler in colour than the commercial gamboge, but when dissolved in turpentine it yields a permanent lacquer with a fine colour.

Ure quotes an analysis showing 89 of resin and 10·5 of gum. A sample of gamboge analysed by Hurst gave: Resin (soluble in ether) 66·05, wax (soluble in alcohol) 4·31, gum 26·03, mineral matter 1·05, and moisture 2·50 per cent.

The resin consisting of gambogic acid, $C_{30}H_{35}O_6$, may be separated from the gum and impurities by digestion in strong alcohol. By evaporating the latter pure gambogic acid is obtained of a deep brown-red colour, which, when pulverized, becomes converted into a beautiful yellow.

Gamboge is therefore a variable mixture of resin and gum. Williams obtained the following figures for gamboge: Acid number 81, ester number 67, saponification number 148, iodine equivalent 115·8, mineral matter 0·48; while Kremel found the acid equivalent to be 100, and the ester equivalent 57. It is scarcely to be expected that a variable product such as this would yield concordant results.

Solubility.—Gamboge is very soluble in ether, less soluble in alcohol. It is often adulterated with starch, sand, and tinctorial barks, a fraud which is detected by digesting the finely ground resin with 60 per cent alcohol and examining the residue with the microscope. Gamboge as met with on the market varies greatly in quality. That from Ceylon, a pseudo-gamboge, is said to be very inferior. The gamboge export of Saigon during last year (1907) amounted to 49 tons, valued at £11,564.

Uses.—Gamboge is used to colour golden lacquers, but it cannot as it stands be used as a pigment except in water-colour painting. Moreover, it is highly poisonous, being a drastic purgative. Gamboge is reddened by acids and bleached by sunlight. Scoffern prepared resinate pigments from gamboge by converting the resin acids into metallic gambogiates. They were exhibited at the 1851 Exhibition.

For the purposes of the analytical research about to be described Tschirsch and Lewinthal cleaned 3 kilogrammes of gamboge and treated it with 95 per cent alcohol, until when tested with water and HCl it no longer gave a turbidity. Whilst the first flow is coloured deep red, the middle flow is yellow, and the last colourless. The alcoholic extracts are mixed, the half of the alcohol distilled off and the filtered tincture mixed with ten times its weight of cold distilled water. By vigorous stirring a uniform yellow emulsion is obtained from which hydrochloric acid separates out the resin in yellow flocks. The filtrate gave with iron chloride a brownish coloration, with lead acetate a white precipitate. Fehling's solution was reduced. The body so obtained from the pure resin forms a light yellow powder which dissolves very readily in alcohol, ether, acetone, toluene, chloroform, benzene, petroleum ether, acetic ether, methyl alcohol, amyl alcohol, and carbon tetrachloride, to a yellow solution. Ammonium potassium and sodium hydroxides, as well as sodium and potassium carbonates, easily dissolve the resin with a

deep red coloration. From this solution it is readily precipitated by acids. Sulphuric acid and nitric acid dissolve the resin likewise with a red coloration in the hot state, yellow in the cold. The resin is absolutely insoluble in HCl and in water. The alcohol solution turns blue litmus red. Attempts to crystallize the resin met with no response. Capillary analysis gave two zones, one well defined and one poorly defined. The purified resin dissolved in dilute potash gave the following precipitate: Strontium chloride, pale yellow; lead acetate, brownish-yellow; iron chloride and ferrous sulphate, black-brown; potassium bichromate, orange-yellow; copper sulphate, grey-green; aluminium sulphate, yellow; nickel chloride, brownish-yellow; cobalt chloride, green; magnesium sulphate, yellow; mercuric oxide, white-yellow; tin chloride, pale yellow; zinc sulphate, yellow. Fehling's solution was reduced. From this property of formed coloured precipitates with salts Tschirsch terms this substance gamboge-coloured resin or chromo-resin. For further purification a large portion of the resin was dissolved in ether and the solution agitated with a weak solution of soda 1:1000. The filtered solution was acidulated with HCl and the precipitate washed and dried. The substance was paler. Its solubility remained. It showed the character of an acid decomposing $MgCO_3$ in the warm. Attempts at crystallization had no result. On dry distilling the pure resin water passes over, then a thick oil with a fruity smell. A sublimate did not occur. Acids of the benzoic acid and cinnamic acid series are thus excluded. On treating the alkaline solution with steam a very peculiarly perfumed substance distils, the smell of which recalls mellisa. On keeping the saponified product for four months the substance changes. At first when separated by sulphuric acid it was red brittle with silky lustre; gradually it assumed a brown colour, and then it passed to a sort of soap, a white greasy mass, and in fourteen days longer it became a granular dark brown soap. Dried, the saponification product forms a light orange-red powder which dissolves in alcohol with a Burgundy red colour and an acid reaction, melting-point 159°-160°. Analysis gave: Found mean of three analyses: C = 58·76; H = 7·39. Calculated for $C_{23}H_{30}O_6$: C = 68·66; H = 7·46.

Treatment of the original with absolute alcohol dissolves the resin which is separated by dry HCl gas. By treatment of the same for a day with cold potash an extract soluble in potash is obtained and another insoluble therein. They cannot be separated from one another by precipitation from the body prepared from alcohol. If a large amount of the body insoluble in potash be suspended in potash and this mixture treated with hot steam the distillate contains ethyl alcohol. Iodine and potash solution give the iodoform reaction. Benzoyl chloride shaken with the fluid gives the smell of ethyl benzoate on introducing HCl. A portion of the substance is etherified whilst the other remains untouched. The

ester formed on treatment with potash is resolved into its components. Melting-point of substance soluble in HCl, 96° to 97° C.; melting-point of substance insoluble in KHO (NaHO and NH_3), 136° to 137° C. Analysis of substance insoluble in KHO. Found mean of four analyses: C = 69·87; H = 7·6. Calculated for $C_{25}H_{32}O$: C = 70·09 per cent; H = 7·48. The portion soluble in potash gave mean of three analyses: C = 67·73; H = 7·59. Calculated for $C_{22}H_{30}O_6$: C = 67·69; H = 7·69 per cent. The potash melt from the data of Hlasiwetz and Barth was made in the ratio of one of potash to three of the resin and fused in an oil-bath in a nickel crucible. The substance melted with a low flame and frothed violently and gave off a peculiar aromatic perfumed vapour. The smell was similar to that on saponification. The froth gradually subsided and the mass boiled quietly. After half an hour it was cooled and dissolved in water. It all dissolved except a small residue. On acidulating with dilute H_2SO_4 a moiety of the resin was precipitated as a black cake with a strong smell of fatty acids of valerianic and butyric acids. The filtrate was shaken five to six times with ether, the ether distilled, the residue heated with water, saturated with soda, again shaken with ether, and the ether partially distilled. It deposited small crystals which were purified by animal charcoal and re-crystallization. The substance had a melting-point of 218° C., was soluble in alcohol, water, and ether. It gave a violet coloration with iron chloride. A crystal laid on a chip of pine and drenched with HCl gave a violet colour. The product separated was thus phloroglucin. The ether was driven off from the fluid, freed from phloroglucin, and the fluid was then acidulated by sulphuric acid and shaken three or four times with ether, the ether driven off and the residue dissolved in water. When the ether was driven off the aqueous solution, it was cooled and precipitated by lead acetate. A voluminous casein-like precipitate fell out. This precipitate contains the two acids, uvitinic and isuvitinic. The lead precipitate was treated with sulphuretted hydrogen, boiled with water, evaporated to a syrupy consistency, and left to crystallize. After prolonged standing it gave small white crystals which were purified by bone-black and re-crystallization. The solution in water reacted acid. Dried at 100° C. the melting-point was 162° C. The substance does not lend itself to analysis. Hlasiwetz and Barth found the values

C = 60·0	60·1	60·4	59·8
H = 4·4	4·8	4·9	4·7

from which they gave it the formula $C_9H_8O_4$, and on confirming this by the ammonium, calcium, barium, cadmium, and silver salts, they gave it the name of isuvitinic acid. They regard it as phenethylic acid 2, methylic acid 1, as a homophthalic acid, or as a phenyl acetic 0, carbonic acid = $COOH{\cdot}C_6H_4CH_2(COOH)_2$. Uvitinic acid is methyl phen 3, 5, dimethylic acid = $C_6H_3CH_3$

$(COOH)_2$. There separated from the liquid from which the isuvitinic acid was separated an amorphous, syrupy pale brown mass, which on solution and treatment with bone-black became more pale but could not be crystallized. The filtrate from the H_2S precipitate was heated to drive off H_2S. There separated after some time a granular, crystalline, reddish-white powder, which blackened at 270° C. and was insoluble in alcohol, ether, and the usual solvents. On re-crystallizing a large crystal, taste and reaction were acid; the low melting-point and its sour taste identified it as tartaric acid. The examination of the fluid left on the expulsion of the ether was now taken in hand. To isolate the fatty acids whose smell had been remarked it was acidulated with sulphuric acid and the acids driven over by hot steam. The resin cake which fell out on treatment with sulphuric acid was repeatedly boiled with water and the fluid treated accordingly. The fatty acids were treated with an excess of calcium carbonate and the calcium salt of the fatty acids dried to a powder. The finally pulverized mass was extracted with absolute alcohol in which the lime salt of valerianic acid and of butyric acid is insoluble, and the acetic acid and formic acid salts insoluble. The alcohol solutions of valerianic acid and butyric acid were mixed and the acids by treatment with dry HCl gas converted into the corresponding esters. The strongly acid solution was neutralized with ignited carbonate of lime and the mixture fractionally distilled. First fraction passed over from 100° to 110° C., second fraction from 100° to 125° C., third fraction up to 140° C. From the second fraction the portion passing over from 119° to 120° was isolated and recognized by its smell and boiling-point as ethyl butyrate. The third fraction, between 134° and 135° C., only gave a small yield, which by the boiling-point and smell was recognized as ethyl valerianate. The residue, insoluble in the alcohol, was tested for formic acid. It did not reduce silver solution. A portion was heated with arsenious acid; it gave off the smell of cacodyl. The calcium salt was dissolved in a little HCl and gave a blood-red coloration with iron chloride, showing acetic acid. The potash melt thus yields phloroglucin, isuvitinic acid, tartaric acid, butyric acid, valerianic acid, acetic acid, an amorphous syrup, a brown mass, and a granular crystalline powder. In the potash melt operation and in the saponification a peculiar smell was given off. To isolate the body generating this smell a mixture of 1 part of the resin and 3 of pulverized potash was dry distilled in an iron retort. The water distilled gave off a strong odour of essence of lemon and melissa. The yield was small, thirty distillations only yielded 7 to 8 grammes of oil. This oil is coloured yellow and is lighter than water. It was salted out with common salt and dried over calcium chloride dissolved in water-free ether and shaken with sodium bisulphite. There was a strong separation of water-white transparent crystals. These were dissolved, decomposed by sulphuric acid, and shaken with ether. On driving off

the ether there remained a somewhat brownish-coloured body with a faint perfume. It could not be fractionated. It resinified on heating. The aldehyde reaction silver mirror gave nothing, nor did magenta decolorized by sulphurous acid. In 5 per cent soda solution or 1 per cent potash it only dissolved slightly. The bulk of the oil dissolved in ether. The ether was driven off by gentle heating and the whole fractionally distilled. The first fraction passed over at 110° to 115° C.; the second fraction at 154° to 171° C.; the third fraction at 171° to 220° C., was very dark brown. Fraction I gave the following on analysis: Found mean of two analyses: C = 76·56; H = 19·22. Calculated for $C_{25}H_{74}O$: C = 76·93; H = 18·97 per cent. Fraction II, mean of two analyses: C = 81·58; H = 12·57. Calculated for $C_{38}H_{70}O_2$: C = 81·72; H = 12·54. On long standing a crystalline body was obtained from the distillate which crystallized from alcohol; had the melting-point of 114° to 115° C. The distillation of gamboge was studied by Tassinari. His procedure was as follows: He used caustic soda and a little water. He found oxygen-free bodies in the distillate with the formula $C_{10}H_{16}$, a limonene. He dissolved the residue in water, but there settled out white flakes which were collected and gave on ignition $C_{10}H_{20}O_2$. On acidulation with HCl a dark resin separated about two-thirds of the gamboge taken. By distilling this substance with zinc dust a mixture of benzene homologues was obtained. The white flakes separated from the resin contained an oily substance from which they were freed by pressure and purified by solution in benzene, from which they crystallized in small crystals. Analysis gave C = 64·43 per cent; H = 5·72 per cent. The composition betokens the formula $C_9H_{10}O_3$, which approaches xylidinic acid: C = 64·43; H = 5·72. The strongly acid residue was neutralized by soda and evaporated to dryness. The residue was like silver acetate. The residue was then extracted with alcohol till colourless. The residue consisted of NaCl and sodium isuvitinate. The isuvitinic acid is dissolved and precipitated as a calcium salt, the ignited ash of which yields lime corresponding to isuvitinic acid. Nothing is obtained from the alcohol distillate. There remains a fluid which separates into two layers, the top dark, the other slightly coloured. The upper neutralized with ammonia and distilled with steam can be extracted with ether, which expelled leaves a thick fluid with a fruity odour, which does not solidify on cooling. It has the character of an aldehyde. Treated with sulphite solution it yields a fluid boiling between 110° and 117° C. of the composition $C_{10}H_{16}O$. It absorbs four atoms of bromine by addition, and passes on oxidation with ammonium potassium silver oxide into a crystalline acid with the composition $C_{10}H_{16}O_2$. Melting-point, 103° to 104° C.

On shaking the concentrated ethereal solution of gamboge with soda, Tschirsch obtained an abundant finely granular red precipitate recognized as a sodium salt. A portion was dissolved in

alcohol and treated with reagents. Lead acetate solution not made with alcohol produced no change, not even on standing. Alcoholic lead acetate at once gave a bulky orange precipitate which was allowed to settle and lead acetate added until no further precipitate was obtained. Dried, it gave a heavy yellow powder that dissolved readily in ether, with difficulty in hot alcohol, and is insoluble in water. On suspending the powder in water and running in a mixture of sulphuric acid and alcohol the lead salt was decomposed; to complete the decomposition, it was left for a long time in contact with sulphuretted hydrogen. The acid went into solution with a red colour and was easily filtered from the lead sulphide. The solution warmed to expel H_2S and treated in the cold with a large excess of water. Yellow-red coloured flakes separate which after appropriate washing were dried at 90° C. in a dessicator. To further purify the substance it was dissolved in dilute potash and precipitated by strong potash. The deep yellow-coloured precipitate was repeatedly dissolved with potash in water and precipitated by HCl. Alcohol, ether, acetic acid, acetone, potash, soda, sulphuric acid, nitric acid, toluene, chloroform, benzene, acetic ether, amyl alcohol, dissolve this substance forming a yellow solution. It is insoluble in HCl and petroleum ether. Melting-point, 129° C. Analysis: Found mean of three analyses: C = 68·73; H = 7·08. Calculated for $C_{23}H_{28}O_6$: C = 69·00 per cent; H = 7 per cent. The acid was named garcinolic acid. The lead salt gave 19·61 and 19·8 per cent Pb. For $(C_{23}H_{27}O_6)_2$ Pb 20·59 per cent Pb is required. Garcinolic acid is monobasic. The filtrate from the lead salt precipitate was still strongly coloured. A test in a reagent glass with water gave an abundant pale yellow precipitate. The separation of the excess of lead acetate was effected by prolonged treatment with H_2S. There was thus separated a bulky dark brown precipitate. The filtrate on expulsion of the H_2S was warmed and on cooling treated with acidulated water. A very finely granular pale yellow precipitate formed which by prolonged washing was freed from H_2S. Dried, it forms a light pale yellow tasteless powder which alcohol dissolves to a yellow solution; likewise ether, acetone, potash, soda, ammonia, toluene, chloroform, benzene, acetic acid, amyl alcohol, and methyl alcohol. Sulphuric acid dissolves it red. It is insoluble in hydrochloric acid and in petroleum ether. It dissolves in potash with a yellow colour, whilst the original material dissolves in potash even in dilute solution with a red coloration. Melting-point, 129° to 132° C. Analysis gave mean of five: C = 70·3; H = 7·41. Calculated for $C_{23}H_{32}O_6$: C = 70·09; H = 7·48 per cent. This body was termed β-garcinolic acid. It forms about four-fifths of the amount of substance taken, that is, the resin treated with soda. Attempts at crystallization have hitherto given negative results. The barium salt of β-garcinolic acid is formed thus: An ethereal solution of the acid is shaken with baryta water in a separating funnel. The whole solidifies on shaking into a soft white gelatinous mass which

in time becomes hard and granular. The excess of baryta water was removed by washing and the substance dried at 100° C. So as to test that no barium carbonate had been precipitated with the salt, a small portion was treated with concentrated HCl, but it gave off no CO_2. Analysis gave: 15·63 per cent and 15·55 Ba. For $(C_{25}H_{31}O_6)_2$ Ba 13·82 per cent Ba is required. The calcium salt is prepared in the same way, only the ethereal solution is shaken with lime water. A red powder forms, insoluble in water, very soluble in hot alcohol. Analysis gave: 5·31 per cent and 5·3 per cent Ca. For $(C_{25}H_{31}O_6)_2$ Ca 4·38 per cent Ca is required. β-garcinolic acid is thus also a monobasic acid. By oxidation with nitric acid it leaves a powder insoluble in ether, toluene, petroleum ether, carbon, tetrachloride, benzene, HCl, chloroform, and acetic ether. Analysis gave mean of four: C = 55·26; H = 5·77 per cent. Calculated for $C_{19}H_{24}O_{10}$: C = 55·34; H = 5·83 per cent. The filtrate contains oxalic acid. A reduction test with β-garcinolic acid with tin and HCl gave a reduction product. Dried, it formed a pale brown light tasteless powder of melting-point 150° to 152° C. The alcoholic solution showed a strong green opalescence. The substance is insoluble in water, petroleum ether, and hydrochloric acid. Analysis gave mean of three: C = 69·39; H = 7·34. Calculated for $C_{16}H_{20}O_4$: C = 69·57; H = 7·25. The acetylization tests gave negative results.

In treating the solution filtered from the α-garcinolic alcohol solution with sulphuretted hydrogen so voluminous a precipitate was obtained that it could not consist of lead sulphide alone. This precipitate was digested with alcohol till it came away colourless. The residue was boiled with alcohol, the deep red solution precipitated with water, and HCl and the red substance dried. Melting-point, 103° to 104° C. Its behaviour with solvents is similar to that of the α and β acids. The substance, however, gives a red-coloured solution with dilute potash. It was termed γ-garcinolic acid. Analysis gave mean of three: C = 71·56; H = 7·37. Calculated for $C_{23}H_{28}O_5$: C = 71·88; H = 7·29 per cent. The extraction of the crude acid, with lead acetate, was repeated, with constant results. With iron chloride all three acids behave similarly. The solution is coloured dark brown and on standing forms a brownish-black precipitate.

The research must be pushed further, until the substance reddened by alkalis is separated from the substance yellowed thereby, which would involve a closer examination of the three garcinolic acids. This, moreover, is rendered very difficult by the impossibility of obtaining the substance in a crystalline form. The formulæ show a mutual relationship and homology :—

(α) Garcinolic acid, $C_{23}H_{28}O_6$
(β) " " $C_{25}H_{32}O_6$
(γ) " " $C_{23}H_{28}O_5$

The residue from the alcoholic extraction of gamboge is a dirty brown pasty mass, which dissolves readily in water to a dirty turbid fluid. Filtration through filter paper is difficult. By use of a Chamberlain clay filter it is obtained as a brown-coloured solution. This solution was with energetic stirring mixed with ten times its weight of a mixture of 90 parts of alcohol and 10 of ether. The gum was not precipitated but formed a white milky fluid with the ether alcohol. After a day's standing a slight precipitate had fallen to the bottom. At last on the addition of HCl the gum separated out. By repeated solution in water and precipitation by acidulated alcohol a gum is obtained which has only a faint yellow impression which was covered round with ether alcohol in drying. The gum dries as a whitish-yellow powder, odourless and insipid. It is soluble in water to a clear but yellow-coloured fluid with an acid reaction. Ignited in a platinum crucible it left no ash. A mixture of alcohol and HCl gives a bulky white precipitate, lead acetate a slight turbidity. With borax solution the gum solution remains clear. Iron chloride on warming gives a dark-coloured flaky precipitate. Fehling's solution was reduced on heating. Ammonium oxalate made no change. Analysis gave mean of three: C = 48·86; H = 6·62. Calculated for $C_6H_{10}O_5$: C = 44·4; H = 6·17. The solution is levo-rotatory. This shows that the arabinic acid of gamboge, like the gum in all gum resins, resembles other natural gums. Nitric acid gives a substance of melting-point 206° C. Analysis shows it to be mucic acid. Found mean of two: C = 34·85; H = 4·6. Calculated for $C_6H_{10}O_8$: C = 34·28 per cent; H = 4·76 per cent. Oxalic acid and tartaric are also produced. The ash of gamboge shows 1·02 per cent, principally calcium and less magnesium.

Gamboge consists of :—

	Per cent.
Gum . . .	16·0
Resin[1] . . .	77

The remainder consists of impurities.

Gurjun Balsam or Cochin-China Wood Oil—Origin.—This oleo-resin, notwithstanding its synonym, has no connexion whatever with Japanese wood oil. The latter is a fatty oil belonging to the class of drying oils. Gurjun balsam is an oleo-resin secreted by different trees belonging to the order *Dipterocarpeæ.*

[1] Of which 10 per cent precipitated by lead acetate, 67 per cent not precipitated by lead acetate.

TABLE LXVI.—TREES AND LOCALITIES YIELDING GURJUN BALSAM.

Species of Dipterocarpus.	Country.
Turbinatus (*lævis indicus*)	E. Bengal, Chittagong, Pegu, Singapore, French Cochin-China.
Trinervis . .	Java and the Philippines.
Incanus . .	Chittagong and Pegu.
Alatus . .	Chittagong, Burma, Tenasserim, Andamans, Siam, and Cochin-China.
Crispalatus . .	French Cochin-China.
Zeylanicus .	Ceylon.
Hispidus . .	,,
Gracilis . .	Java.
Littoralis .	,,
Retusus (*Spanoghei*)	,,

Habitat.—These *Dipterocarpeæ* grow in the forests of mountainous regions, and more especially on the borders of the clearances.

Yield.—The collection of the oil is one of the chief industries of French Cochin-China, where the trees are now felled in a systematic manner under Government supervision. The annual value of the oleo-resin of a *Dipterocarpus* in that country is estimated at about 16s. to 17s., and the trees continue to yield for about 100 years.

Collection—Forestry Technology.—The oil is collected in the following manner: The woodman first of all makes a round hole in the wood (with an auger) about 2 inches in diameter and reaching to within a short distance of the opposite side of the tree. It is at the mouth of this hole that the font is made to receive the oil. At this point a deep, almost horizontal cut is made in the tree by means of an axe, and higher up another verticle cut meeting the other at an acute angle. A sort of font or basin-shaped hole is thus scooped out of the trunk of the tree about the height of a man from the ground where the oleo-resin collects. When the collection of the resin commences, glowing charcoal is placed in the font or leaves saturated with oleo-resin, and inflamed; the surface of the wood chars and the fluid oil commences to flow. The fire is then extinguished, and three to four days afterwards the oil is collected. At intervals of three to four weeks the charred surface of the font is chipped off and the fresh surface again fired. The same font may be fired eight to ten times, and it is not uncommon to find upon the same tree and at the same height four or five cuts, each of which are exuding oleo-resin.

The oil is collected by means of a sort of spoon, formed of meshes of cocoa-nut, and fixed to a bamboo handle; occasionally by means of a gutter with a wide mouth, from which the liquid runs into a receptacle at the bottom of the tree. Some species of *Dipterocarpeæ* secrete balsam spontaneously from a cut made on the trunk which is collected in the cold. This "cold-drawn" quality is much

esteemed by the Annamites for the manufacture of lacquer. The collection of balsam constitutes the principal if not the sole occupation of the Annamites of the province of Ben Hoa. The product is of a mixed character, varying much in character and quality owing to the resin of different species being collected and stored in the same vessel.

The oil resembles copaiba in smell, flavour, and therapeutical properties, but it imparts no unpleasant smell to the breath. It is completely soluble in benzene, cumol, chloroform, and carbon disulphide, and partially in the other varnish solvents, e.g. ether, petroleum spirit, carbon disulphide; alcohol dissolves 90 per cent of the resin. According to Daliere it contains 2·46 per cent of an ether calculated as the acetate of a sesquiterpene alcohol; its rotatory power is very variable—35° to 106°.

Commercial Varieties.—Two qualities of oleo-resin are met with: (1) *Pale Yellow* (*Blonde*). The product principally of *Dipterocarpus turbinatus*, and which on standing separates into two layers. The upper layer is clear limpid amber, yellow, and slightly fluorescent. The lower layer is very abundant, viscous, and of a greyish-white colour. (2) *Black*. The product principally of *Dipterocarpus alatus*. On standing it separates into a thick, viscous, and very fluorescent upper layer, deep brown-red by refracted light, greenish by reflected. The lower dark greenish-black layer of less bulk separates more rapidly. The density of these oleo-resins is not definite; it would appear to oscillate between 0·960 and 0·966. The pale oil is always the lighter in gravity. Both the blonde and the black oleo-resin when distilled yield a volatile oil which has been rectified over calcium chloride.

Rectification—Fractionation of Pale Yellow Oil.—A litre of blonde oil mixed with 6 litres of water yields 290 grammes of a straw-yellow volatile oil, lighter than water, whilst a white material occupies the space between the water and the oil, which would appear to be the hydrate of the volatile oil. This hydrate is decomposed at a slight heat (176° C.) in contact with calcium chloride.

By fractional distillation, M. Rigal has obtained 242° C. as the point at which the liquid boils. The different fractions pass over as under:—

1st fraction between 258° and 262° C.
2nd fraction between 267° and 275° C.
3rd fraction between 284° and 295° C.

The third oil is greenish in colour.

Black Oil Fractionation.—The black oil, 320 grammes per litre, commences to boil at 248° C., and yields:—

1st fraction between 252° and 257° C.
2nd fraction between 260° and 262° C.
3rd and final fraction between 262° and 266° C.

Properties.—These oils rotate the plane of polarization differently. This is due to the fact that they are the product of different species.

(French and American spirits of turpentine—one obtained from *Pinus maritima* and the other from *Pinus taeda*—behave similarly.) They detonate with fuming nitric acid. Nitric acid gives a violet coloration, sulphuric acid a purple-red, hydrochloric acid a violet-red. Iodine attacks them energetically but without explosion.

Java Copal.—Dieterich recently examined a new fossil-copal from the interior of Java, the extensive deposit in a lignite seam being to be worked if worth while. The rounded elongated lumps the size of walnuts like unwashed, unscraped kauri have not the goose skin of Zanzibar copal. The milky internal mass in a thin weathered outer layer has a glossy conchoidal fracture, is easily rubbed down to a brownish-grey powder containing black granules, lignite particles, and pyrite crystals left behind as a black tinsel of metallic lustre in the insoluble residue. The copal does not soften thick yellow-brown tar, with an empyreumatic smell. The residue in the retort consisted of 13·87 per cent of a black carbonaceous mass which caught fire when the retort burned through. It yielded tar on extraction with ether. This yellow extract turned a fine reddish-yellow on concentration, and exhibited a green fluorescence which was not altered by acid or alkali. The total loss on dry distillation amounted to 14·43 per cent of the copal, the greater portion consisting of the uncondensable white fumes given off at the outset. Fractions I to V, which at first were cloudy from the presence of water, gradually became perfectly clear on standing, whilst Nos. II to V darkened in colour. So far as possible determinations were made of the coefficients of refraction, density, and Hübl-Waller iodine value of each fraction, the resulting figures being given below:—

TABLE LXVII.—PHYSICAL AND CHEMICAL CONSTANTS OF JAVA COPAL (DIETERICH).

Fraction.	Refractometer Index.	Coefficient of Refraction.	Specific Gravity at 15° C.	Iodine Value (6 hrs.).
I	80° @ 17½° C.	1·4803	—	—
	41° 11 @ 17°	1·4812	—	—
II	35° 50 @ 17°	1·5116	0·9210	87·24-96·58
III	—	—	0·9280	113·48-120·68
IV	—	—	0·9200	98·10-102·68
V	—	—	0·9805	42·68

Conclusions.—The copal is evidently a hitherto unknown product, which does not seem to have anything in common with the other varieties of copal, even that from Manila. It is of a fossil character, as is shown by the adherent impurities. It is probably far superior to Manila and kauri copal, but inferior to and softer than Benguela copal. The value is about 8d. a lb., as compared with 6½d. for Manila and 2s. 6d. for best Zanzibar.

As the sample was small the tests had to be confined to hardness, melting-point, specific gravity, presence of sulphur,

nitrogen, bitter principles, ash, moisture, volatile acids, and ethereal oils, with determination of acid, ester, and saponification values, exact determination of solubility in various solvents, behaviour on dry distillation, and examination of the fractions. Examination by Tschirsch's method had to be delayed till the promised larger sample is received.

Hardness.—The copal is easily scratched by calc-spar and copper sulphate, but only partly so by rock salt. and is therefore harder than Indian or Manila copal. *Melting-point.*—Placed in a capillary tube, sealed at one end and plunged in a bath of sulphuric acid, intumescing point 160° to 170° C.; incipient fusion 175° C.; complete fusion 178° C. As good copal melts at a higher temperature, the sample cannot be classed very high in this respect. *Density.*—The specific gravity of the cleaned lumps is 1·033 to 1·041. *Sulphur Test.*—The melt with soda and saltpetre, dissolved and saturated with nitric acid, gave a decided sulphuric acid reaction with barium nitrate; but the sulphur is evidently derived from the embedded pyrites. *Nitrogen Test.*—Negative results. Ash 2·44 per cent; colour, reddish-brown; composition, mainly ferric oxide. *Moisture* at 100° C. for two to three hours, 0·265 per cent; under prolonged heating the weight increased again. Bitter principle, by the Tschirsch and Niederstadt method (extracting repeatedly with boiling water, and concentrating the aqueous solution), revealed no bitter taste, nor could any trace of bitter principle be detected with ferric chloride, lead acetate, or tannic acid. No ethereal oil or volatile acids occurred in the products of steam distillation. Acid value (hot), 4·55 to 5·07. Saponification value (hot), 14·54 to 15·92 to 16·56 to 18·03. Ester value (calculated), 9·99 to 12·96. Hubl-Waller iodine value (twenty-four hours' reaction), 50·86 to 54·66. *Solubility.*—The quantitative results are given, for undried material, in the following table:—

TABLE LXVIII.—SHOWING THE SOLUBILITY OF JAVA COPAL IN VARIOUS SOLVENTS.

Solvent.	Loss at 100° C. per cent.	Soluble Calculated. 100° C. per cent.	Soluble Found. 100° C. per cent.
Alcohol (95 per cent)	82·58	17·16	15·86
Ether (sp. gr. 0·72)	41·63	58·10	62·91
Acetone	80·61	19·12	26·24
Chloroform	2·59	97·14	101·80
Benzol	3·92	95·82	97·64
Carbon disulphide	5·84	93·90	97·59
Methyl alcohol	92·97 / 0·265	6·76	7·61
Petroleum ether	2·24	97·50	96·52
Chloral hydrate (60 per cent)	95·29	4·44	—
,, ,, (80 per cent)	90·76	8·98	—
Dichlorhydrin	73·86	26·88	—
Epichlorhydrin	53·96	45·78	—
Oil of turpentine (ordinary)	2·58	97·16	—

It is evident that the soluble matter could not be determined directly owing to oxidation and increase in weight of the evaporation residue in drying, hence the insoluble percentage is given and the soluble calculated. By reason of its insolubility this copal belongs to a high class. The solubility after melting could not be determined owing to lack of material. According to Mauch, Java copal being insoluble in chloral hydrate should be classed along with the true copals.

Dry Distillation Products of Java Copal.—The remainder of the sample, about 75 grammes, was subjected to dry distillation in a tubulated 200 c.c. retort of Jena glass, heated up to 360° C. on a sand-bath, and after that over a naked flame, until nothing but a carbonaceous residue was left in the retort. No sublimation in the neck of the retort or in the condenser tube could be detected at any time during the distillation. At first the copal powder turned very brown, with considerable liberation of uncondensable white, pungent fumes and water vapour. Up to 80° C. no distillates passed over from the melted mass. At 100° C. there were distilled the first drops of a pale yellow, cloudy, thin oil, smelling of turpentine. At 120° C. (Fraction I) about 1·07 per cent distilled over, this portion containing much water. Fraction II passed over, up to 280° C., as a dark brownish-yellow, highly refractive empyreumatic oil, to the extent of 15·97 per cent of the copal. Fraction III (280° to 300° C.) forming 22·61 per cent, was darker and more empyreumatic, smelling strongly of ethereal oil of wormwood, but the smallness of the quantity precluded any decisive test as to the actual presence of that oil. Fraction IV (300° to 360° C.) was a reddish-brown oil, with pungent, empyreumatic smell, and equal to 19·03 per cent of the copal. The final fraction (VI) came over as a thick greenish-brown oil, smelling of oil of turpentine. The quantity was equal to 12·93 per cent of the copal. There was also about 0·4 per cent of a

Xanthorrhea Resin.—The Xanthorrhea or grass-trees are *Juncaceæ*, confined to Australia and Tasmania. They are plants with a short, thick ligneous stem, generally simple, terminated by a tuft of long leaves about 3 feet, with cutting edges. The inflorescence emerging from this crown of leaves consists of a bunch of sessile flowers supported on a rigid peduncle of 5 to 8 feet in length. The three most interesting species are *X. hastilis R. Br.*, stem short; likewise *X. Australis R. Br.*, and the *X. arborea R. Br.*, the stem of which, on the contrary, rises some feet in height. From the trunk of these trees there flow in virtue of a continuity of accidents or by incisions a resinous substance which concretes in the air in contact with more bulky pieces. Sometimes the fragments detach themselves spontaneously and collect at the foot of the tree, where they are often found buried, semi-fossilized. The resin is collected thus, according to Maiden: The pieces of resin are detached with a pick or a hatchet and collected on a cloth. The product is sifted,

then assorted and put on the market. The *X. arborea* yields abundant bulky masses of a reddish-brown resin, brittle, with a brilliant fracture which pulverizes readily and is reduced to a brown colour like Terra di Sienna.

The resin of *X. Australis* exudes at the base of the trunk near the roots in globular irregular masses, brownish or of a homogeneous ruby-red which exhales an odour of benzoin. The product of *X. hastilis* has also this same odour of benzoin. All these resins by exposure to light exhibit a superficial red-brown layer which encroaches on the paler internal colour. The resin of the *Xanthorrhea* is very soluble in ether, which would appear to be its best solvent. It is soluble also in alcohol and potash. It is insoluble in benzine, turps, and toluene. To obtain the pure product it is pulverized and exhausted by ether. The filtered solution is of a fine gold yellow. The residue remaining on the filter consists almost exclusively of plant debris. After evaporating the solvent on the water-bath a yellowish-red resin is obtained, exhaling the odour of benzoin. Stenhouse was the first to examine the resin so purified. He found that its potassic solution treated by hydrochloric acid gave a precipitate of benzoic and cinnamic acid, and that it produced picric acid when treated with nitric acid (Hlasiwetz and Barth, "Bull. Soc. Chem.," I, 1867, p. 431). When this resin is oxidized by potash a large amount of para oxy-benzoic acid is obtained. But Maiden fixes this amount at 8 per cent. During the reaction an aromatic vapour and much volatile fatty acids are given off. The ethereal extract furnishes by crystallization para-oxybenzoic acid. The mother-liquor of this extract contains a little resorcin as well as a pyrocatechic compound of para-oxybenzoic acid. A weight of 18 oz. of resin, about 530 grammes, yield 36 grammes of para-oxybenzoic acid, 4 grammes of resorcin, about 5 grammes of pyrocatechin, and 6·5 grammes of soluble acid. According to Hildebrand, yellow accroides contain cinnamic and paracumaric acids free and combined with Xantho-resino tannol, styracin, para-oxybenzoic aldehyde, and probably small amounts of phenyl propyl cinnamate as well as traces of vanilla. When this resin is distilled, 0·37 per cent of an essential oil is obtained, which possesses an odour of storax. *Red Accroides, Earth Shellac.*—This resin is derived from *Xanthorrhea Australis R. Br.*, also from *X. tateana* and *X. arborea.* Likewise the ruby-red basal plates from *X. quadrangularis.* By examination under the microscope this resin shows no crystals, only the resin from *X. Australis* contains a small amount of a double refractive substance.

Red accroides differ in composition from the yellow variety in containing paracumaric acid but no cinnamic acid; parabenzaldehyde is present, but no vanillin styracin nor the phenol propyl cinnamate. The greater bulk of the resin consists of an ester of paracumaric acid conjugated with erythro-resino tannol. The tannol resin alcohol has the formula $C_{40}H_{39}OH$ and is readily

nitrated into picric acid. Benzoic acid, but only in the combined state, is also present. The *Xanthorrhea* resins thus belong to the same class as Peru balsam, storax, and benzoin.

Minor Use for Red Accroides.—A concentrated solution of the red resin containing a little castor oil or copaiba balsam has a magnificent red colour which is employed to coat the windows of photographic laboratories so as to exclude the active rays.

Yellow Gum Accroides.—Botany Bay resin, blackboy gum, grass-tree gum, resina lutea novæ belgiæ, the product of *H. hastilis*, contain, according to Hildebrand, free acids—cinnamic and paracumaric. The latter is also present in the form of an ester combined with Xantho-resino tannol, an alcohol with the formula $C_{43}H_{49}OOH$. This ester constitutes as much as 80 per cent of the resin. Xantho-resino tannol is an alcohol containing a hydroxyl group. No methoxyl group could be detected by the Zeiss method. The behaviour of the acid and benzoyl derivatives pointed to the presence of a hydroxyl group only. This resin alcohol can be converted by direct nitration into picric acid. In addition to the above, styracin, cinnamic acid, phenol propyl cinnamate, para-oxybenzaldehyde, and possibly vanillin, are also present. This product is but little used, and only fetches about £4 a ton in London. In Australia, however, European workmen and Chinese use it in making certain varnishes. Although produced so abundantly in Australia these were, until comparatively recently, practically unknown in this country. Even now they are only occasionally imported, though it is true they, to a certain extent, could replace dragon's blood, gamboge, and other tinctorial agents in the colouring of pale lacquers.

CHAPTER XVII.

JAPANESE, CHINESE, AND BURMESE LACQUERS.

JAPANESE lac or *urushi* is the milky juice of the *Rhus vernicifera*, D.C. (*Rhus Vernix Thunb*), the *urushi-noki* of the Japanese, a tree cultivated at different altitudes at Dewa, Aizu, Shimodzuki, Hiroshima, Yoshino, in the neighbourhood of Tokio, etc. The *Rhus vernicifera* is confused with the "tree of heaven," the *Ailanthus glandulosa*, cultivated in many European localities, but having nothing in common with the real Japanese varnish-tree, which, nevertheless, may itself be likewise cultivated in Europe. In fact, in 1886 Prof. Rhein brought some stocks from Japan which he planted in the Botanic Garden of Frankfort. These plants in a few years developed into trees which produced normal fruit. Seeds were thus obtained which when sown produced hardy young plants; a gum-resin juice may even be extracted from the trees thus acclimatized. But it remains to be seen whether or not the product is identical with that elaborated in Japan. The *Rhus vernicifera* is a small tree, with large, alternate, imparipinnate leaves, consisting of six or seven pairs of leaflets, with short leaf-stalks, membraneous, oval-oblong, glabrous above, with veins covered with short hair underneath. The flowers are polygamous, forming terminal or axillary panicles, hairy, much exceeding the half of the length of the leaves. The glabrous calyx comprises five short oval obtuse divisions. The five oblong petals are three or three and a half times longer than the limbs of the calyx. The five rudimentary stamens in the female flowers have each a filiform filament twice as long as the oval, dorsal-fixed introrse anther. The ovary is surmounted by three short styles. The fruit is a slightly flattened drupe containing one seed with a membraneous ligument. Another species of *Rhus* is also cultivated in Japan, the *Rhus succedanea*, L., the *Hazé* or wax-tree, but for the sake of its wax, contained in the mesocarp of the fruit. This white vegetable wax was formerly highly prized, but is now much less esteemed than the varnish. The *Rhus vernicifera* may also yield wax, but to the detriment of the varnish, because, if the tree produces fruit, the secretion of varnish is diminished. The production of these two substances is mutually antagonistic, and as the varnish is the most valuable and scarce product of the two, the fructification of the trees, so injurious to its secretion, should be prevented.

Culture.—Much information in regard to the cultivation of the *Rhus vernicifera* is to be found in a communication (of which there is a French translation) by LeonVan de Polder, published in the "Koloniaal Museum de Haarlem," No. 3, September, 1892, on the Japanese varnish-tree. The varnish-tree is included, with the tea-plant, the paper-tree, and the mulberry, amongst the "four useful shrubs" treated of in the seventh volume of the "No-gigo-dzen-sho," or "Complete Treatise of Agricultural Occupations," in ten volumes with supplement, published by Myasaki Yassada and Kalbara Rakuken. In fact the varnish-tree is cultivated in a very careful and methodical manner in Japan. The tree is reproduced in three different ways: (1) By root-buds; (2) by slips from the stem; (3) from seed. (1) *By root-buds.*—From October to March the roots

FIG. 32.—*Rhus Vernicifera.*

of the vigorously growing trees are lifted (choosing those 3 c.m. (say 1⅛ inch) in circumference). They are cut into pieces of 30 c.m. (say 12 inches) or even 15 c.m. (say 6 inches). Then, in the month of March, choosing preferably a sandy soil, alongside the embankments, roads, rivers, these buds are planted. The cutting is planted on the slant, leaving 3 c.m. (say 1⅛ inch) above the ground. In the month of May the young buds begin to sprout. A slightly different method consists in conducting these propagating operations in a nursery, in the month of March, and transplanting them to the open field in the month of April of the following year. Such plants yield varnish in 55 years. But the long and costly budding process is but little used, the more so as in stripping the tree of its roots it may be seriously injured. (2) *By slips.*—Cut from the stem of adult trees. The plants reared from slips are also so far developed after five to six years as to

yield varnish. It will be seen that this is a convenient method which should be adopted where practicable. (3) *By seed.*—This is the most practical and most general method. It will therefore be given here in detail. At the end of October, or in November, when the fruit is quite ripe, it is gathered and crushed in a wooden mortar, so as to detach the two exterior envelopes of the pericarp, leaving the kernel covered with the waxy matter contained in the mesocarp. They are then washed in an alkaline lye of potash or soda. The nuts which float on the liquor are worthless, and are rejected. The kernels are then packed in straw sacks and preserved during winter. In the beginning of March the sacks, with their contents, are steeped in running water for ten days to hasten germination. If there be no running water in the neighbourhood, care is taken in the beginning of winter to inter the sacks containing the kernels under 12 c.m. (say 4½ inches) of earth, in a spot neither too dry nor too moist till the spring, when they are then sown, directly, in a nursery. The seed is sown in the middle of March. At the end of the preceding summer a good soil has been chosen as a nursery seed bed and carefully tilled to a depth of rather over a foot, and to which human excrement or horse dung has been applied. In autumn the soil is again tilled. In spring, at the time of sowing, the ground is tilled afresh, during which it is formed into raised beds, 75 c.m. square and 18 c.m. in height. The seed is sown on these beds at the rate of 45 to 54 seeds per bed. They are covered by a layer of soil about ¾ inch in thickness, or with straw, and watered every evening. At the end of three weeks, when the seeds have started to sprout, the straw is removed. The young plants must then be protected from the sun. Weeds are carefully removed. At the end of September the protection from the sun is removed. In the following March the plants, 9 c.m. (3½ inches) in height, are transplanted into another soil 15 to 20 c.m. (say 6 to 8 inches) apart. Those under 9 c.m. (3½ inches) must wait. After two years, in the month of October, they are definitely transplanted into the open field; the young trees are then 25 to 30 c.m. (10 to 12 inches) in height. In another method the young trees are first transplanted when two years old and definitely transplanted when five years old and 90 c.m. (3 feet) in height in the middle of March. The varnish-trees are planted 1½ metres (say 5 feet) apart on the flanks of the mountains, on the embankments, in trenches along the roads, etc. Sandy soils are best. Trees raised from seed yield varnish when ten years old when 4 to 5 metres (13 to 16 feet) high. But the yield is most abundant when they are between twenty-five and thirty years old. It appears that there are two varieties of varnish-tree, a thin- and a thick-barked variety, and that it is the latter which yields most varnish. The variety known as *naqui* yields the best quality lacquer. It is known by its leaf, longer and thinner than the others, and its thick bark. Trees with thin leaves as well as thin bark yield the least

lacquer. The species called Sekiboka or barren tree is the worst, yielding little or no lac. It is difficult to recognize except by an incision in the bark. If the bark be hard it is a Sekiboka.

In several Japanese provinces the male stocks are said to be carefully differentiated from the female stocks, the former alone yielding varnish, the latter only yielding wax-producing fruit. The *Rhus vernicifera* being polygamous these assertions are not quite correct. It appears, in fact, that under certain conditions the inflorescence may be predisposed to produce male flowers, and in other cases female flowers. The latter are soon transformed into fruit rich in wax. Now, as it is admitted that the yield of varnish is in inverse ratio to that of wax, the male stocks would be the real varnish-tree. It is probable after what has been said of the determinism of sexuality amongst plants, that the greater the vitality of the plant the greater is the abundance of female flowers. In any case, the Japanese seem to modify their treatment of the tree according to whether they wish it to produce varnish or wax. In order to produce female stocks they use a larger quantity of manure. However, some growers say they make no difference in the treatment of male and female stocks, and that it would be difficult to say which of the two yielded most varnish. The harvest commences at the end of May, or in June, and ends in October. The prime quality is collected between June and October. After the middle of October the exudation diminishes and the quality deteriorates. This constitutes the second quality and does not dry so quickly. The third quality, got from cut branches, is inferior. The really superior varnishes seem to be got in July and August. The trees are tapped as follows: At a height of 30 or 40 cm. (12 to 16 inches) from the ground the surface of the bark over a certain space is scraped with a tool called a *koshiguara*. In the middle of the cleaned strip a horizontal incision of 10 mm. is made with another tool called a *kakigama* in about three points round the tree. The varnish exuding from these small incisions is removed with the *kara* and placed in a bamboo tube which the collector carries. Then new, longer but parallel incisions are made above the first, proceeding in this way from below upwards. The varnish is collected as the work proceeds and placed in the bamboo pot. Then the workman passes to another tree. When he has gathered the product of five or six trees he returns to the first and collects the lac which has exuded from the original incisions. As the varnish soon assumes a brown or a blackish colour no time should be lost in collecting it. The incisions should be about 5 mm. apart and should not penetrate further than the bark so as to husband the vital powers of the tree. New incisions are made a little higher up, and even on the big branches, according to the vitality of the plant. When all the trees are tapped the branches are lopped off and cut into sections 75 cm. (say 30 inches) long and the sections made into bundles of twenty. They are placed upright

in water to three-quarters of their height for six to eight days, when the bundles are taken out of the water and incisions made on each fragment about an inch apart, and the varnish which exudes is collected. The collector taps about 200 trees daily. The yield of a tree depends on many circumstances—its age, vitality, the soil, the variety to which it belongs, etc. But speaking generally, it may be said that a tree of 15 to 21 cm. in circumference (6 to 8 inches) may yield in a season from 90 to 95 grammes of varnish (say 3¼ oz.). In more favourable circumstances as much as 150 grammes (say 5 oz.) may be got. It has been observed that it is after rain and in dull weather that the exudation is most copious. When it rains the rain deteriorates the varnish, and penetrating by the incisions may injure the tree. It is therefore better to stop collecting the resin in rainy weather. The varnish collected in bamboo pots is run into small barrels called *oké*, and finally into casks, where it may be stored for ten years without alteration. To estimate the lac crop, trees are incised here and there and the crop estimated from the flow. This is termed *kokui*. The quality is tested as it flows from the incisions. In a good season it is sweet, in a bad one bitter.

The lac gathered from the commencement of June to the 10th of October, the period in which the tree produces the most, is the best. This is the first quality. From the 10th of October to the end of the month the lac diminishes in quantity from day to day and the quality is not so good. This is the second quality. When it is very hot the juice runs from the trees like oil. Nevertheless, not much is produced. The weight is very much less, but the quality is good. In rainy weather, and especially when it is misty after a rain, the crop is very much more abundant, but the lac is somewhat inferior. The juice which runs from the incisions is collected and put into a small vat. The lac thus obtained by steeping the branches is the third quality, and is called *seshima urushi*.

The first operation to which the crude natural varnish is subjected before being used as a lacquer is to evaporate the water which it contains. To effect this the varnish is filtered through cloth and the filtered liquid collected in a wooden vessel in which it is constantly stirred in the sun by a workman. The water may also be evaporated from the varnish in a porcelain vessel over a gentle wood-charcoal fire. In either case the varnish becomes gradually darker in colour. When on spreading it on a wooden slab the lustrous layer is seen to dry sufficiently quick, it is again filtered through cloth packed with waste. The lacquer after evaporation and filtration is mixed with different substances, such as lampblack, vermilion, indigo, orpiment, so as to produce the various varnishes used to lacquer objects in Japan, black, red, green, and violet lacquer, etc. Some of these mixtures are even, it would appear, kept secret by those in the trade.

The varnish with an *urushi* base dries rapidly when applied in a humid atmosphere and very slowly in a dry one. On the other hand, they all darken in the sun and even in diffused daylight. The varnishes are therefore applied in badly lighted or even dark rooms, and in the intervals between work they are kept in perfectly dark, humid, and unventilated apartments. Japanese varnishes are not so transparent as European, but soften less on heating and are more elastic and durable. The fastidious methods of lacquering now in vogue or those which have been in vogue in Japan are too detailed for minute description. The process was conducted in accordance with very minute and detailed rules on which the perfection of the lacquer depended, and entailed much time and laborious manipulation. The modern Japanese could hardly submit to retain such costly processes. The ancient lacquers are therefore infinitely superior to those of the present time, as is attested by the following fact. The steamer "Nile" bringing back the artistic objects which were exhibited at the Vienna Exhibition foundered in water about 11 fathoms deep, near Cape Idson. The Japanese Government engaged divers to recover what they could of the cargo, and, *inter alia*, the lacquered articles, which had remained fifteen months at the bottom of the sea. *Whilst all the old lacquers were in a state of perfect preservation, the recent ones were irretrievably ruined!*

The chief varieties of lac used by the Japanese are:—1. *Ki urushi.*—The lac or varnish as it comes from the tree. 2. *Tatchiki urushi.*—Is lac filtered through a coarse sieve or paper (?) *Ki-sho-mi* of Rein.—This filter paper is the Yashino gani. 3. *Seshime urushi.*—The filtered lac to which a greyish tint has been given by filtration, evaporation and stirring. 4. *Djohana urushi.*—Prime quality black lac. 5. *Djotchu or Djonaka urushi.*—Second quality black lac. 6. *Naritate urushi.*—Another second quality black lac. 7. *Naka nuri urushi.*—Black lac used as inner coat. 8. *Koiro urushi.*—Black lac for last coat. 9. *Nasidji urushi.*—A yellowish or brownish lac imitating the rind of a pear. Gold dust is mixed with it. 10. *Shu urushi.*—Red lac. 11. *Shunkei urushi.*—A light brown lac. The lac called *hana urushi* is composed of 375 parts of lac, 75 parts of oil, and 7½ parts of iron filings. To make the *shu urushi*, or red lac, the flower of the *Gardenia florida* is steeped in water, then dried completely in the sun and added with oil and vermilion to the lac. In preparing the black lac the *shunkei urushi* is exposed to the sun in a round tub, whilst a workman constantly stirs it up with a spatula. At the end of a day the lac has turned entirely black. The operation is facilitated by adding a little *tetsuko* or iron filings in rice vinegar. The following day the lac is filtered through filter paper to take out all dust, sand, or other foreign matter that may have fallen in. To prepare a red or a yellow lac it is merely necessary to add a red or yellow powder to this same *shunkei*, stirring constantly so as to have a thoroughly intimate mixture.

With these coloured lacs the true colour is hardly produced until the lacquered article has been allowed to dry for two or three weeks.

In lacquering the necessary instruments are :—1. *Shirato.*—A polishing stone. 2. *Honokisumi.*—Charcoal made from the wood of the *Magnolia hypoleuca*, a large Japanese tree. 3. *Roïrosumi.*—Cherry-tree charcoal. 4. *Tsunoko.*—Polishing substance obtained by burning the antlers of the stag. 5. *Ionoko.*—A fine powder which remains on the sharpening stone after having sharpened a knife. 6. *Shibu.*—The sap of the *diospyras kaki*. 7. *Djïnoko.*—Burnt potter's clay. 8. *Gofun.*—Another sort of burnt potter's clay. 9. *Haké.*—The lacquering brush. 10. *Héra.*—A spatula of flat thin wood. In lacquering, a first coat of No. 3 (p. 243) is given, when dry a second coat is given of 3 mixed with 5 *Sabi*, applied with the *Héra* 10 (p. 244). A third coat, mixture of 3, 5 and 7 (p. 243), is then applied with the *Héra*. The fourth coat, *nwasabi*, is like the third, but less of 5 is used, being more fluid it is applied by brush. After each coat the object is polished with the *Shirato*. It is then covered with 6 (p. 243), mixed with soot, and when dry rubbed with sandpaper. Coloured coats according to tint desired are then given. Two, three or four of these coats are applied before final one, and between each the article is polished by magnolia charcoal and then with cherry-wood charcoal. It is often a month before the true lustre shows.

Tschirsch and Stevens investigated the composition of Japanese lac. They obtained the following results : Matter soluble in alcohol, 72·4 ; soluble in water, 4·05 ; moisture, 21·20 ; and insoluble matter, 2·35 per cent. The portion soluble in alcohol, termed urushinic or laccic acid by Yosihda and laccol by Bertrand, was found not to be a pure substance, but was separated into two fractions, the one soluble and the other insoluble in petroleum ether. The portion soluble in petroleum ether was found to consist of three products : a gum, a toxic, or poisonous substance, and an enzyme. Free acetic acid was also found to be a constituent of the lac. On exposure to air lac hardens and blackens, this being due to the action of an oxydate-laccase on the resins. If the lac be sterilized by heat this hardening does not take place, and if the lac be sterilized and then treated with alkali it blackens immediately, but it does not harden on exposure. Two bodies separated from lac, named urushin and oxyurushin, contain nitrogen, the figures for the latter corresponding to the formula $C_{162}H_{138}N_2O_{10}$, but neither urushin nor oxyurushin shows acid functions like the true resins. The toxic or poisonous body present in lac is non-volatile ; contrary to the statements of some chemists, it has not yet been obtained in a pure state, though it has been separated as an oily liquid. It has a powerful action on the skin, causing acute irritation and inflammation.

Japan Lac.—The juice of the lac tree (*Rhus vernicifera*) has been further examined by K. Miyama, who found that this material, treated with alcohol and filtered, and the alcohol removed, left

about 80 per cent of crude so-called "urushinic acid," which was purified by repeated treatment with petroleum spirit. The filtrate was evaporated, first at ordinary pressure, and then under diminished pressure, leaving a residue which was found to distil *in vacuo* to the extent of about 41 per cent without decomposition. The distilled portion consisted of a light brown viscous liquid, having a specific gravity at 21·5° C. of 0·9687, and dissolved easily in the ordinary solvents. It contained no nitrogen, and gave the same reactions as the undistilled product. From an examination of this product Miyama came to the conclusion that it contained two phenolic hydroxyl groups, and that therefore the name "urushiol" would be more appropriate than "urushinic acid". The distilled substance has practically the same composition as the undistilled product, which gives carbon 79·65, hydrogen 9·75 per cent, and it may be that the portion which did not distil over is a polymerized substance of high molecular weight.

Kisaburō Miyama, in his "Recent Research on the Composition and Technical Value of Chinese Lacquer," prefaces his account of his investigation and description of his methods by the following forcible comments: "Japanese lacquer, or *urushi*, is a milky juice exuding from the trunk of the lacquer-tree or *Urushihaze* (*Rhus vernicifera*, D.C.), and is very widely employed in the manufacture of lacquered wares in Japan. The milky juice, called raw lacquer or *ki-urushi*, loses its moisture on exposure to the sunlight or on warming, and becomes a brown oily liquid. For practical purposes the moisture of the raw lacquer is expelled, and oils, colouring matter, etc., are added; the lacquer thus obtained is called finished lacquer, or *seishi-urushi*. The raw lacquer consists mainly of a brown liquid, gum-arabic, enzymic nitrogenous matter, and moisture. The brown liquid, the predominant and most important constituent of the lacquer, was named *urushic acid* by O. Korschelt and H. Yoshida, who investigated the subject some twenty years ago. According to these investigators, the brown liquid is a monobasic acid of the formula $C_{14}H_{18}O_2$, and is oxidized to oxyurushic acid, $C_{14}H_{18}O_3$, on drying. However, the series to which this acid belongs has not yet been determined, and, furthermore, its behaviour is different from that of acids. As a matter of fact, characters common to organic acids are not found in it, and so it cannot be proved to be an acid. Recently, Tschirsch and B. Stevens suggested that it was a resin of the empirical formula $C_{102}H_{138}N_2O_{10}$ and named it *urushin*. However, the presence of nitrogen is very doubtful, and also the sample analysed by them seems to have been already oxidized by drying, because its oxygen content is far different from that of urushic acid, and such an analytical result, I believe, cannot be expected from any sample of carefully prepared urushic acid. Therefore, the problem of ascertaining the chemical constitution of the principal constituent has been especially interesting to me.

"The principal constituent, the so-called *urushic acid*, is prepared best from the raw lacquer by extracting with absolute alcohol and removing the alcohol by distillation. The brown liquid thus obtained reddens a blue litmus paper, but after repeated washing with a large quantity of hot water, the acid reaction is transferred to the washings, and the brown liquid no longer reddens the test paper. The washings contain a little acetic acid and an extractive matter which resembles gum-arabic in its appearance, but differs from the latter in its composition and solubility in absolute alcohol. Old samples of the brown liquid are partly changed to a thick liquid insoluble in petroleum ether. Therefore, the constituent for investigation was purified by repeated washing with a large volume of boiling water, and by extracting with ten times its volume of petroleum ether. It is not certain that the constituent thus purified is a strictly pure compound, but since no other method of purifying has been found, it is assumed to be a pure compound. The raw lacquer for investigation was collected in the province of Yamato under special supervision, and was warranted free from admixture. The principal constituent consists of carbon, hydrogen, and oxygen, and the percentage composition is as follows:—

	C.	H.	O
1	78·48	9·55	11·97
2	78·03	9·65	12·32
Average	78·25	9·60	12·15
$C_{34}H_{50}O_4$	78·10	9·65	12·25

"The molecular weight determined by Raoult's method is 509. From the above result it appears that the molecular weight of the constituent corresponds to $C_{34}H_{50}O_4$.

"*Summary.*—The principal constituent of the lacquer is *an aromatic compound* containing carbon, hydrogen, and oxygen, the latter existing in the state of *hydroxyl*. It shows phenolic character in its behaviour, and contains at least two *phenolic hydroxyl* groups in the ortho-positions. It is *an unsaturated compound* and absorbs eight atoms of halogens in the molecule. Therefore, the principal constituent is *a polyhydric phenol* containing unsaturated radicles in its side chains, and I propose for it the name *urushiol.*

"*Properties of the Lacquer.*—The raw lacquer consists of moisture, urushiol, gum-arabic, nitrogenous matter, and some added oils. The compositions of the specimens of superior lacquer are as follows:—

TABLE LXIX.—COMPOSITION OF SAMPLES OF HIGH CLASS JAPANESE LACQUERS.

Specimen.	Moisture.	Urushiol.	Gum.	Nitrogenous Matter.
No. 1	9·32	86·97	2·46	1·25
No. 2	12·21	80·63	5·69	1·47
No. 3	10·94	84·53	3·25	1·28

"The specimens of raw lacquer found in commerce vary to a considerable extent, their quality depending mainly on the locality and the period in which they are collected. The specimens collected from the same lacquer-tree at different periods gave the following compositions :—

TABLE LXX.—COMPOSITION OF LACQUERS FROM THE SAME LACQUER TREE AT DIFFERENT PERIODS.

	Moisture.	Urushiol.	Gum.	Nitrogenous Matter.
Sakari-urushi (From July 11 to August 31.)	17·81	77·63	2·62	1·94
Urame-urushi (From September 21 to October 10.)	22·61	70·20	4·74	2·45
Tome-urushi (From October 11 to 31.)	23·30	66·66	7·57	2·47
Seshime-urushi (Collected from the branches during November.)	27·62	64·14	6·46	1·78

"*Sakari-urushi* which is collected during the heat of summer is of the best quality, and when freed from moisture it contains urushiol 94·5 per cent.

"The lacquers imported from China and India are far inferior in quality, as is shown in the following analyses :—

TABLE LXXI.—COMPOSITION OF CHINESE AND INDIAN LACQUERS.

	Moisture.	Urushiol and Oils	Gum.	Nitrogenous Matter.
Chinese lacquer (superior)	20·37	70·02	7·72	2·34
" " (middle)	30·74	55·88	11·78	1·60
" " (inferior)	36·85	36·88	23·55	2·72
Indian " (middle)	33·38	26·39	37·78	2·45

"Among the constituents of the lacquer the most important is urushiol, and the more of this it contained the better is its quality. Gum-arabic is of no value, and the more of this there is the more inferior is the quality. The nitrogenous matter is a constituent necessary for the drying of the lacquer, which, without it, is impossible. It differs from albumen in its composition, and consists mainly of an oxidation enzyme.

"The lacquer spread in a thin layer dries rapidly in a damp atmosphere and hardens to a lustrous coating which is extremely stable and resistent to various solvents and chemicals. For the drying of the lacquer, the presence of moisture and a temperature between 10° and 30° C. are necessary ; for this reason the lacquer dries more slowly in a dry season than in a wet season ; and in the winter than in the summer. The drying of the lacquer is much

retarded by warming to a temperature above 50° C., and its drying quality is entirely suspended by keeping it at a temperature of 70° and 80° C.; in this respect the drying of lacquer differs from that of drying oils. Drying at a high temperature, however, by no means requires the presence of moisture or enzymic nitrogenous matter. In a steam-oven or an air-oven with a temperature above 100° C., the lacquer dries within four or five hours, and the higher the temperature is the more rapidly it dries. For instance, at 150° C. it dries within thirty minutes, and at 180° C. within ten minutes. Lacquer which has lost the drying quality, or even urushiol which does not dry by itself, dries readily at a temperature above 100° C.

"*The Increase in Weight of the Lacquer on Drying at an Ordinary Temperature.*—When the lacquer dries, its weight is more or less increased by the absorption of oxygen. However, the increase of weight during the period in which the lacquer is hardening to a solid film is not considerable; but the increase continues at least for three months and becomes a considerable amount. This fact is shown by the following experiments: The raw lacquer spread in a thin layer inside a beaker was dried in a dessicator over night and the lacquer thus freed from moisture was weighed; next, it was dried (*hardened*) in a damp cupboard for two days, and after drying in a dessicator over night was weighed again. The same operation was repeated several times and the increase of weight was observed. Lacquer, 0·6066 grammes; lacquer, after drying for two days, 0·6167 grammes; lacquer, after drying for ninety days more, 0·6415 grammes; increase of weight in ninety-two days equals 0·0349 grammes, equals 5·75 per cent of the lacquer. The lacquer completely hardens in the first two days, but the increase of weight does not cease then.

"*Technical Analysis of the Lacquer.*—The value of lacquer is dependent upon the durability, the transparency, the colour, the lustre, and the smoothness of the lacquer-coating, and upon the viscosity and the drying time of the lacquer. The chemical analysis of the lacquer generally employed is as follows: About 1 gramme of the lacquer is dissolved in 30 c.c. of absolute alcohol, filtered through a tared filter and well washed with absolute alcohol. From the filtrate and washings the alcohol-soluble matter (a mixture of urushiol and oils) is determined after evaporating the alcohol. Next, the residue on the filter is washed repeatedly with boiling water; and from the washings and the insoluble residue, the water-soluble matter (gum-arabic) and the nitrogenous matter are respectively determined. The difference between the weight of the sample and the sum of the alcohol-soluble, the water-soluble, and the nitrogenous matter is taken as moisture. The constituents of raw lacquer to be estimated are moisture, urushiol, gum-arabic, nitrogenous matter and some added oils; and those of the finished lacquer are, in addition to the above, colouring matter, drier, and some other added substances. Owing to the constant admixture of

oils in the lacquer, it is desirable to have a complete method of separating the urushiol from the oils and other added substances. In the usual method of analysis, however, it is almost impossible to separate the urushiol from the oils, therefore I tried to find a new method of determining the urushiol.

"*New Method of Determining Urushiol.*—Urushiol is detected by the following tests: With ferric chloride a highly diluted solution of urushiol gives a green colour which turns red on the addition of sodium carbonate. With ammoniacal silver nitrate, it forms a silver mirror in the cold. With barium hydroxide, the solution deposits a characteristic green precipitate. Among these, the reaction with barium hydroxide is the most important, and is employed for the estimation of urushiol. If a slight excess of a barium hydroxide solution is dropped into an alcoholic solution of urushiol, with the previous addition of a few drops of phenolphthaleïn solution, a green precipitate of barium salt is deposited, and the supernatant liquid is coloured pink. Therefore, urushiol may be determined volumetrically with a standard barium hydroxide solution. The barium salt is more or less decomposed when water is present; for instance, if a titrated urushiol solution which is not yet alkaline is diluted with a small quantity of water, it becomes fairly alkaline. Thus the quantity of barium hydroxide absorbed by urushiol varies with the strength of the barium hydroxide solution and the quantity of alcohol used in the titration. The following table shows the results of the titration of 1 gramme of urushiol with barium hydroxide solutions of various strengths:—

TABLE LXXII.—RESULTS OBTAINED BY TITRATING URUSHIOL WITH N $\frac{N}{4}$ $\frac{N}{8}$ $\frac{N}{10}$ BARIUM HYDROXIDE SOLUTIONS.

Exp.	Alcohol Used.	$Ba(OH)_2$ sol. Required.	Calculated as N $Ba(OH)_2$ sol.
(1)	250 c.c. abs. alcohol	7·0 c.c. N. sol.	7·0 c.c.
(2)	250 " " "	24·6 " $\frac{N}{4}$ "	6·15 "
(3)	250 " " "	41·5 " $\frac{N}{8}$ "	5·19 "
(4)	250 " 97 per cent alcohol	51·5 " $\frac{N}{10}$ "	5·15 "

"From the above experiment it appears that the barium hydroxide solution and the alcohol to be used in the titration must be of a definite strength, and the quantity of alcohol must be in a definite proportion relative to that of the urushiol to be titrated. In practice, it is convenient to use 200 to 250 c.c. of absolute alcohol for every gramme of urushiol, and the quarter-normal barium hydroxide solution in the following way: About 0·5 gramme of the urushiol

under examination is dissolved in 100 to 125 c.c. of absolute alcohol with the addition of a few drops of phenolphthalein solution, and titrated with the quarter-normal barium hydroxide solution, until the supernatant liquid gives a pink colour. By this method six samples of urushiol were titrated with the following results:—

TABLE LXXIII.—RESULTS OF TITRATION OF SIX SAMPLES OF URUSHIOL.

	Substance Taken.	$\frac{N}{4}$ $Ba(OH)_2$ sol. Required.	Normal $Ba(OH)_2$ sol. for 1 gramme Urushiol.
Urushiol (1)	0·2465 gramme	6·05 c.c.	6·135 c.c.
Urushiol (2)	0·3051 „	7·50 „	6·146 „
Urushiol (3)	0·3074 „	7·55 „	6·138 „

	Substance Taken.	$\frac{N}{4}$ $Ba(OH)_2$ sol Required.	Urushiol Found.
Mixture of { *Urushiol* 69·50, *Linseed oil* 30·50 }	0·1777 gramme	3·05 c.c.	69·93 per cent
„ „ { *Urushiol* 59·87, *Mixed oil* 40·13 }	0·4923 „	7·25 „	59·95 „
Impure Urushiol from an inferior lacquer	0·3074 „	6·65 „	91·16 „

"Since the first three experiments show that 1 gramme of urushiol requires 6·14 c.c. of the normal barium hydroxide solution, the percentages of urushiol in the impure samples are calculated from the results of titration according to the formula: Urushiol $= \frac{V}{6 \cdot 14} \times 100$ where V = volume in c.c. of the normal barium hydroxide solution required for 1 gramme of the samples. In the above titration, the oils remain indifferent and the quantitative determination of urushiol is effected. The quantity of the barium hydroxide absorbed by urushiol increases as the strength of the barium hydroxide solution increases, and gradually approaches the theoretical number calculated from the equation:—

$$C_{34}H_{50}O_4 + 2Ba(OH)_2 = C_{34}H_{46}O_4Ba_2 + 2H_2O.$$

But it falls to one-half of this number when the precipitated barium compound is decomposed with a large quantity of hot water and then titrated back with a standard hydrochloric acid.

"The composition of the barium compound, precipitated from the urushiol solution with barium hydroxide, varies with the quantity of the precipitant and the condition of preparation; but certainly the salt is an urushiolate which has absorbed a large quantity of oxygen. For instance, the compound precipitated from the urushiol solution with 75 per cent of the theoretical amount of barium hydroxide and washed with absolute alcohol gives the following composition:—

C.	H.	O.	Ba.
51·40	6·15	16·74	25·71

"These figures correspond to the formula $Ba_{1\cdot5}C_{34}H_{47}O_{8\cdot3}$, showing that the composition of the urushiolate is indefinite. The urushiolate absorbs oxygen rapidly, and the original urushiol cannot be obtained on decomposing it with acids. When the newly precipitated barium urushiolate is thrown into a large quantity of water without delay, and well washed, a different kind of barium salt is obtained, which gives the following composition :—

TABLE LXXIV.—COMPOSITION OF BARIUM URUSHIOLATE.

		C.	H.	O.	Ba.
No. 1 (Air-dried)	(1)	56·44	6·71	17·25	19·60
	(2)	56·15	6·64	17·56	19·65
	Mean	56·30	6·67	17·40	19·63
No. 2 (Air-dried)	(1)	56·06	6·60	18·07	19·27
	(2)	56·00	6·69	18·02	19·29
	Mean	56·03	6·65	18·04	19·28
$BaC_{34}H_{48}O_8$ requires		56·54	6·70	17·73	19·03

"This barium salt gives an almost definite composition corresponding to the formula $BaC_{34}H_{48}O_8$, and contains eight atoms of oxygen in one molecule, that is to say, twice the number of oxygen atoms contained in urushiol. Barium urushiolate is insoluble in petroleum ether and cold alcohol, but soluble in chloroform."

Japanese Lac.—A further communication on this subject is made by Miyama, who states that urushiol has the composition $C_{20}H_{30}O_2$, and is a divalent phenol. Then follows a long communication on the action of ozone on the dimethyl ether, with the formation of bodies which he terms "oxonides," the examination of which is stated to throw much light on the constitution of this compound.

"*Analysis of Raw Lacquer. Moisture.*—About 1 gramme of lacquer filtered through a cotton cloth is weighed into a beaker and dried on a water-bath until the liquid becomes transparent, and then put into a steam-oven for half an hour. The loss of weight gives the amount of moisture. *Urushiol.*—Lacquer free from moisture is dissolved in 10 c.c. of absolute alcohol, and after standing for half an hour transferred to a tared filter, and washed with absolute alcohol. The filtrate and washings are divided into two equal parts, one of which is used to determine the alcohol-soluble matter and the other to titrate urushiol with the standard barium hydroxide solution. *Oils.*—The difference between the alcohol-soluble matter and urushiol gives the amount of oils. *Gum-arabic.*—The residue on the filter is extracted with boiling water and the aqueous solution is evaporated to dryness and weighed. *Nitrogenous Matter.*—The insoluble residue on the filter is nitrogenous matter; it is weighed after drying.

"*Analysis of Finished Lacquer. Moisture.*—Moisture is determined in the same manner as in the case of raw lacquer, but it is better to take about 2 grammes of the sample. *Urushiol.*—Lacquer free from moisture is dissolved in 20 c.c. of absolute alcohol and after

standing for an hour is transferred to a tared filter, and the alcohol-soluble matter is determined. In the case of black lacquer, one or two drops of the half-normal hydrochloric acid must be added, or the lacquer is not easily dissolved. The alcohol-soluble matter is washed first with hot water, next with warm sodium carbonate solution, and then with hot water again, and re-dissolved in alcohol. The alcoholic solution is divided into two equal parts, one of which is titrated with the standard barium hydroxide solution in order to estimate the urushiol, and the other is evaporated on a water-bath and weighed to determine the sum of urushiol and oils. *Oils.*—The amount of oils is obtained by subtracting that of urushiol from the sum of urushiol and oils. *Gum-arabic.*—This is determined in the same way as in the case of raw lacquer, but all water-soluble admixtures, such as honey and maltose, come under this head. *Nitrogenous Matter.*—This is determined in the same way as in the case of raw lacquer; but all insoluble admixtures come under this head. *Ash.*—Ash is determined by igniting 1 gramme of the lacquer in a basin. Inorganic substances contained in the ash often suggest the driers or some of the admixtures in the lacquer."

Chinese Lac is extracted from a tree which the Chinese term Tsi-tse-chou. But it is hard to say exactly what species is meant. Loureiro ("Flora Cochinensis," 1790, p. 337) describes the varnish-tree under the name of *Augia Sinensis*, and looks upon it as distinct from the *Rhus vernisc* of Linneus, which yields *Japanese lac*. According to Pierre, Loureiro seems to have described as his *Augia Sinensis* or *Cay Son* both *Rhus succedanea*, L., which grows in Tonkin and China, and some species of *Melanorrhea*, which is not *M. laccifera*, since he speaks of 100 stamens in the flower, and as to the fruit and the leaves they refer to a *Rhus*. R. Smith inclines to think that Chinese lac is the product of a *Melanorrhea*, as it must be observed that the Burmese lacquer, yielded by the *M. usitata*, much resembles Chinese lacquer, and appears to be even an identical product. Moreover, it is not impossible for the Chinese to exploit as varnish-trees both a *Rhus*, which would appear to be the *Rhus vernicifera* itself, or an allied species, and a *Melanorrhea* allied to the *M. laccifera* of Cochin-China or the *M. usitata* of India and Burma. However that may be, varnish-trees are distributed over the equatorial regions of China, in the provinces of Se Tchouan, Kouang-Si, and Yunnan. Father d'Incarville published a very detailed examination of the subject in question in the "Memoirs of the Academy of Science," Paris, 1760, III, p. 177, and although the information given therein is nearly 150 years old, it may yet be safely quoted as giving the present facts of the matter, so much is the worship of tradition and the spirit of conservatism a distinctive feature of the Chinese character. The varnish-tree grows wild on the mountains. It is easily reproduced from slips, and grows equally well on the plain as on the mountain. When cultivated the tree yields better varnish and more abundantly. If cultivated

the varnish is collected three times a year, but only once a year on wild trees. The extraction process differs from that in vogue in Japan. Three incisions are made on the tree in the form of a triangle with the base at the bottom. At the base of this triangle a shell is fixed to intercept the resin flowing from the two lateral incisions. These incisions are made from below upwards. After three hours the shells are detached and the varnish collected into bamboo pails hanging from the loins by scooping it out of the shell with the finger, previously moistened with the tongue to prevent the varnish adhering. Many use a wooden spatula moistened with water. The varnish is stored in barrels, the mouths of which are closed by a sheet of paper made of hemp fibre. The varnish which flows from the wild tree is collected in a very crude way. Cuts are made at different heights on the tree and the varnish is collected at the foot. The product eventually reaches the manufacturing towns in barrels containing 24-30 kilogrammes. At Canton, according to Natalis Rondot, an eye-witness, three sorts of lac are to be distinguished. The most valuable has a dark *café au lait* colour inclining to red. It comes from Se Tchouan. The second quality from the same source is paler. The third quality is still paler, that is, a light *café au lait* or a greyish-rose. Brown colours, darkening rapidly in the air, are thus the most esteemed. These are said to be the fine and superior lacquers. However, the members of the Lyons Commission protest against this current opinion, and assert that the palest lac is the best in quality, and it is by an error of appreciation and ignorance that the Chinese value chocolate-coloured lacquers more highly than pale ones. Formulated in this absolute manner, this assertion does not appear admissible, because it is in contradiction with the experience of several centuries of the Chinese artisans whose skill is legendary. The Chinese are in no whit inferior to the Japanese in the minute care which they bring to bear on the lacquering of articles. The resplendent lustre and durability of the lacquers used by the Chinese in the decoration of articles of *virtu*, ornaments, etc., have for centuries been the admiration of Western Europe. At first sight their method would appear to be altogether different from our own. But on closer inspection it will be found that the principal of both is identical, the only real difference being in the material used. The lacquer is not employed in the raw state except for ordinary varnishes, when several successive coats are given to the article, drying after each coat in a dark and humid atmosphere. But for fine varnishes the lacquer is treated as follows: It is heated in a porcelain vessel over a gentle fire, taking care to stir the mass with a spatula until all the water is evaporated. The evaporation is stopped when the liquid flows drop by drop and slowly. It is now filtered. This purified varnish is not used directly; it is generally mixed with tung oil and different pigments to produce red, yellow, green, and violet lacquers. The drying properties of the tung oil have been

increased by exposure to air and sunlight. Father d'Incarville distinguishes three kinds of varnish—*Nien-tsi*, *Si-tsi*, *Kouang-tsi*. The varnish is first reduced to half its original bulk by exposure to the sun, then thickened with about ¾ oz. pig's gall thickened in the sun. After stirring this with the varnish for a quarter of an hour they add about ½ oz. of Roman alum per lb. of pure varnish, stirring until violet bubbles appear. This varnish is Kouang-Tsi. For black varnish they add ivory black or hartshorn black and tea oil rendered drying by boiling with arsenious oxide or sulphide. Further, as a vehicle for pigments the Chinese use a special varnish called Hoa-Kin-Tsi, formed by a mixture of equal parts Tshao and of Kin-Tsi. They made the first by adding Tung oil to Kouang-Tsi and the second by the addition of the same oil to Si-Tsi, and in both cases a certain quantity of camphor. The varnishes thus made are applied in a very judicious and systematic manner. Thus the varnishes instead of being mixed are applied one above the other and gold bronze strewed between the two layers, thus producing the pretty groundwork on objects of art and of *virtu*. The varnish is repeatedly filtered before use, four or five times in succession, so as to obtain a perfectly homogenous fluid which is applied in very thin successive contiguous layers. The Chinese, according to Father d'Incarville, coloured their varnishes as follows: Yellow, *orpiment*; red, *vermilion* or *safflower*; violet, *Tseche*-violet stone; green, a mixture of *indigo* and *orpiment*; white, by incorporating *silver leaf* in the body of the varnish.

The varnishes now current in China are black varnish and red varnish. The first consists of lacquer boiled with white lead, the second of this same boiled lacquer and finely ground vermilion, titrated together in a mortar. Both are filtered through cloth lined with a layer of raw cotton. In all these mixtures the lacquering process is identical. The object to be lacquered should be very smooth and dry. The first coat is applied and exposed over a fire of wood-charcoal or to the sun for a few minutes and allowed to dry for twenty-four or forty-eight hours. A new coat is applied and so on, according to the number of coats to be given. The varnishing is done with a pad. Before applying a new coat the previous is rubbed down with a polishing stone. Seven to eight coats are given to a well-lacquered article. The lacquering is done in workshops closed in every direction, so that the work may not be spoiled nor the surface granulated by dust or by small insects. It is a peculiar fact that darkness and humidity are essential to the drying of a lacquer; the floor of the drying apartments has therefore to be moistened in too dry weather. But however carefully and minutely fastidious the Chinese artisans may be over their work, Chinese varnishes have neither the beauty nor the lustre of Japanese lacs. In regard to this point it is narrated that the celebrated Chinese Emperor, Kanghi, as great a patron of the fine arts as a fine connoisseur himself, acknowledged the superiority of articles

varnished with Japanese lac. "The application of the varnish," said His Majesty, "requires a mild, fresh, humid, and serene atmosphere; that of China is rarely mild, and almost always hot or cold or charged with dust and salts. That is the reason why articles varnished in China have not got the lustre of those of Japan, which being in the middle of the sea has an air more adapted to dry the varnish than to wrinkle or tarnish it." This Imperial opinion, however, is not shared by the reporter of the Lyons Commission, who thinks that if the Chinese be inferior to the Japanese in the lacquered goods industry, it is because their lacquer is not very pure in consequence of shameful adulteration. The most remarkable difference between Chinese and European varnish is the fact that the quicker European varnish dries the more brittle does the coating become, and the greater is its tendency to scale off. The Chinese varnish, whilst drying quicker, does not possess this fault. Fine quality Chinese varnish sells from 1s. 2d. to 2s. per lb., inferior quality from 11d. to 1s. 2d. per lb.

A uniform surface is got by the application of a coat of lacquer which is pumiced when dry. The article is covered with a paste of linseed and glue. The first coat of lacquer is applied on this and at once covered with a very fine linen cloth, which must be made to adhere to it in every point. When this is dry it serves as the foundation for the thirty-three subsequent coats. No intermediate coat can be applied until the previous one has been (1) thoroughly dried in the damp room, dust being rigidly excluded, and (2) has been polished with a fine-grained stone, the final polish being got by rubbing with hartshorn ash. The gilding or silvering of a lacquered article, according to Quin, is done as follows: A special, very fine textured paper, treated with a mixture of glue and alum, is used for drawing the design which has to be reproduced in foil. The design is then traced on the back of the paper with a rat-hair brush charged with previously boiled lacquer. The paper is then applied to the article and made to adhere by rubbing with a whalebone or minoki-wood spatula. When it is removed the design may be developed on the surface of the object by dusting on very lightly a white powder by means of cotton-wool. The same piece of paper may be used for any number of objects, but requires fresh use of the rat-hair brush about every twenty times. The parts to be gilt are now gone over with a hare-hair brush dipped in raw lacquer. This is a most delicate operation, and of course the lacquer must not go over the boundaries of the design. The metal to be used is now applied in fine powder by aid of a pad of cotton-wool. The excess of metal is removed by a brush made from the long winter hairs of a white horse. In the case of a larger article only a portion of the object is gilded at a time, and the article is kept from dust in a tightly closing cupboard. When the gilded surfaces are dry the design is covered with transparent lacquer and the gilding of another portion is begun. Care, how-

ever, must be taken that the parts previously gilded are perfectly dry. When the gilding is finished all the gilt parts are rubbed down with a piece of camellia wood-charcoal and finally polished with hartshorn ashes and oil applied with the fingers.

The Black Lacquer of Indo-China is the product of the *Melanorrhea laccifera*, Pierre, which the Annamites call Mu Cay Son or Mu Son and the Cambodians, Dom chhoeu Kruol. Pierre, in his "Flore forestière de la Cochin Chine," describes this species as follows: Tree, 15-20 metres; leaves, oboval, rounded or attenuated rounded, terminated in a point at the base and decurrent on the very short, flattened petiole; entirely glabrous, coriaceous, furnished with eighteen to twenty-four pairs of side as well as tertiary veins; venation more raised above than below; clusters shorter or longer than the leaves, naked at the base, with ramifications somewhat far apart, papillary or puberulent. Pedicels longer than the flower; calyx, glabrous; petals, entirely hairy outside; stamens to the number of thirty; ovary pedicel, pubescent; ovary, glabrous; drupe, spherical, longer than its pedicel. The *M. laccifera* grows in loamy soils all over Cambodia, in the forests of Tayninh, the provinces of Saigon and Bien-hoa in Lower Cochin-China. It has now retired to the mountains and become rare on the plains. This tree grows very rapidly during the first twenty years of its life, after which its growth slackens. It is easily reproduced from seed. Pierre ("Bulletin of the Linnean Society of Paris," 2 December, 1885) has observed plants reared from seed in rows 3 feet apart. When seven years old the trees are 3 metres (say 10 feet) high and their trunk is 8 cm. (3 inches) in diameter. Their juice may be extracted two years previous to this. The *M. laccifera* is thus tapped for its resin when five to six years old. The Kmers call the varnish which it yields *Morac* or *Mairac*. The incisions are made from December to April, during which period the amount of lacquer extracted may amount to 2 litres. The extraction process is simple: The tree is beaten with a bruising instrument and nodes of bevelled bamboo inserted as collecting pots and allowed to remain for two months. The liquid thus collected may be kept perfectly well for several months in perfectly closed vessels, and that is the way in which it is sent to market. Pierre declares that it can be kept for two years by covering it with a layer of *Dipterocarpus* oleoresin (gurjun balsam, so-called wood oil), filling the vessels full and carefully luting them. When it exudes from the tree this lacquer is yellow or reddish, then it becomes a deep black. The composition of Mairac is unknown, but very probably it does not differ essentially from that of Japanese lac. One thing is certain, that like the latter the Indo-Chino lac contains a volatile oil which renders it corrosive when fresh, but as it ages it loses this corrosive nature when time is allowed for the corrosive principle to be dissipated by volatilization. *Preparation of the Lacquer for Varnishing.*—In Cochin-China Cay Son lacquer is mixed with gurjun balsam

in the proportion of 2 parts of lacquer to 1 part of wood oil. The mixture is first exposed to the sun to give it the necessary fluidity. It is then passed through a sieve to free it from extraneous matter. Purified in this way it forms a very brilliant varnish. According to a note published by the "Revue Coloniale" of 19 May, 1895, a Chinese lacquerer found that candle-nut oil (*Aleurites moluccana*, Wild), after having been reduced by boiling, possesses analogous properties to a quick-drying oil of Chinese origin and which the Chinese of Cochin-China use in making their varnish. Specimens of wood varnished with lacquer, collected in the forests of Tayninh, and candle-nut oil are, it would appear, deposited at the Saigon Chamber of Commerce. Now the oil used in China for this purpose is extracted from the seed of a tree which is no other than an *Aleurites—A. cordata*, Stend (*Elaeococca verrucosa*, A. Juss), that the Chinese call Tong Tse Chou or Oil Tree, and the Japanese Wu Lung. It is not therefore surprising that candle-nut oil from an allied species should have analogous drying properties and should be capable of being utilized in making these varnishes. Moreover, according to Lemarié ("Rev. Cult. Col.," 5 September, 1899), the *Aleurites cordata* grows wild in the forests of Tonkin. It is the Cay Trau or rather the Cay Dan Son of the Annamites. But the colonists of Tonkin confuse it with the *A. moluccana*, under the name of candle-nut tree, a name which only belongs to the latter species. Moreover, trau oil has many analogies with candle-nut oil. It is yellowish, viscous, combustible, and much more quick drying. It is used with the lac after boiling. It is the wood oil of the Anglo-Chinese market, not to be confused with gurjun balsam.

Use and Commerce.—Indo-Chinese lac is used by the Cambodians to varnish *de luxe* carriages, fancy boxes of betel wood, altars, the doors and columns of pagodas, etc. The Annamites and the Chinese also use it to lacquer their furniture and other articles made of wood. No trade is done in this lacquer with Europe, but it sells very dear in China, where an outlet is found for it, no matter what may be the amount dispatched. Its price is about 15 piastres the picul of 60·4 kilogrammes (say 141 lbs.).

When the Annamites set to work to varnish an article, they at the outset fill up all the crevices and pores of the wood so as to produce a uniformly smooth surface by applying a priming of lacquer with a very short, close brush, after which a thick coat of lacquer, mixed with a white unctuous clay found at the bottom of ponds, is applied, and when dry the surface is well pumiced. If the article be carved, clay cannot be used. After pumicing the article has a flat appearance and is given a third coat of lacquer, which imparts a lustrous but not varnished appearance. Like the Chinese lacquer it only dries in moist air. After the third coat has dried all that has to be done is to varnish the article and give it any desired colour, and this coloured "enamel" is applied in one

operation. Except by the use of metallic powder or foil the lacquer can only be coloured black, brown, or red, thus:—

(1) *Black.*—Turpentine resin is heated above its melting-point for twenty minutes and then run into three times its weight of lacquer. Copperas and green vitriol is added at the same time and the mixture stirred for at least a day, sometimes longer. (2) *Chestnut Brown.*—The same process as above, substituting vermilion for one-half of the copperas. (3) *Red.*—The lacquer, first stirred for six hours, is mixed with hot trau oil (wood oil) and the stirring is then continued for a day. Vermilion is then added, and must be of the best quality so as to yield a permanently brilliant colour. This finishes the lacquering, but on gilded parts the leaf is applied in a mixed vehicle of *trau* oil and lacquer, all mixtures of these two vehicles being carefully filtered through cotton-wool resting on a silk cloth before use. The final coat is applied some months after the gold leaf, but if tin or silver leaf has been used it can be applied in a few days, and imparts a gold-like appearance to these two metals. The tint if too red at first becomes quite brilliant in a few months.

Burmese and Siamese Lacquer.—This lacquer differs very little from that of Cochin-China and Cambodia. It is the product of the *Melanorrhea usitata*, Wild, a tree of about 80 feet in height, growing in Burma, the Malacca Peninsula, and Siam. The young trees, leaves, and infloresences are covered with hair. The leaves have the same shape as the *M. laccifera*, but as just said they are *hairy*; moreover, the secondary veins number twenty-eight to thirty pairs. The infloresences equal the leaves, the pedicels are as long as the flowers. The calyx is *hairy* like the corolla, whilst it is *glabrous* in the preceding species. There are thirty stamens or more. The ovary is *hairy* and the drupe subglobular. As a matter of fact, the *M. laccifera*, with the exception of the corolla, is a generally *glabrous* plant, whilst the *M. usitata* is *hairy*. This tree is exploited for its lacquer in Burma and Siam. As in Indo-China, the extraction process is very simple. Nodes of bamboo are cut bevel-shaped, implanted in the bark, and left there for a longer or shorter time. A hundred of these bamboo recipients may be fixed in the trunk and large branches of the tree. The lacquer is collected in Burma during the time the tree is deprived of leaves, which is also the period when the lacquer flows most abundantly. A tree may yield annually 1½ kilogrammes (say 3¼ lb.) of crude varnish, which as it exudes from the tree is of a lead-grey colour, but is not long in becoming, in contact with the air, a brilliant black. The lacquer may be used for the same purposes as the Cochin-China lacquer. An interesting account of the Burmese lac is given by P. Sing in the "Indian Forest Records" for 1909, pp. 287-308. This product is obtained from *Melanorrhea usitata*, a tree closely related to *Rhus vernicifera*, from which the Japanese lacquer is obtained. The method of collection is to make a V-shaped

cut in the stem, the sap being collected in a bamboo cup fixed below. The crude varnish is purified by straining through a cloth. The lacquer is a thick, greyish fluid, with a specific gravity at 20° C. of 1·0016 (Japanese lacquer = 1·0020). It was analysed by the methods of Ishiwatsu and Yoshida and was found to consist of a resinous extract soluble in hot alcohol, albuminous matter soluble in water and precipitated by boiling, gummy substances, a small quantity of fatty matter, and a residue insoluble in alcohol and water. The principal constituent of the lacquer was found to be "urushic acid" ($C_{14}H_{18}O_2$). The following analyses show the composition of Burmese lacquer compared with the Japanese lac:—

TABLE LXXV.—COMPOSITION OF BURMESE AND JAPANESE LACQUERS.

	Burmese Lacquer.		Japanese Lacquer.	
	1.	2.	1.	2.
Alcoholic extract (urushic acid)	86·24	83·24	85·15	80·00
Gummy matter	3·08	3·52	3·15	4·69
Oily matter	*nil*	0·53	?	?
Residue or diastatic matter	1·71	2·14	2·28	3·31
Moisture and volatile	8·97	10·57	9·42	12·00
	100·00	100·00	100·00	100·00

Burmese lacquer sets hard when exposed to a cool, moist atmosphere, but it does not set by exposure to sunlight, heat, or dry air. It appears from the researches of Miyama that "urushic acid" contains two phenolic hydroxyl groups, and is, therefore, a polyhydroxyphenol and not an acid; it gives a greenish colour with ferric chloride, and forms weak compounds with alkalis and alkaline earths, which are easily dissociated on solution in water. The drying of the lac is due to oxidation, and is apparently caused by an enzyme, which has been called "laccase".

NOTE.—*Perilla Oil used by the Japanese to add to their Lacquer.* —Mention has been made of tea oil and tung oil being used by the Chinese to add to their lacquer, but the Japanese also use an oil, viz. perilla oil, the product of a *labiate* plant, *perilla ocymoides*—sown in April, blossoming end of September, and ripe by middle of October—which is extensively grown in China and Japan.

Tea Oil.—The tea oil used by the Chinese is made from the *fruit* of a peculiar kind of a tea tree like our plum tree, the fruit resembling our chestnut, except that the outer husk does not bristle with points. The fruit of the Tongchou, from which they extract Tongyeou, also resembles it.

CHAPTER XVIII.

MANILA COPAL—MASTIC—SANDARAC.

Manila Copal.—In view of Dieterich's research on Java copal, which he claims to be a fossil copal, it will be desirable here to complete our account of Tschirsch's research on Manila. Tschirsch and Koch separated 4 per cent of a resin acid by ammonium carbonate from solution of soft Manila copal in ether. About 1 kilogramme of the copal in solution was submitted to fifty extractions. The resin acid separated by hydrochloric acid dissolved slightly in the usual solvents but scarcely dissolved in petroleum ether. In ethyl-methyl alcohol it deposited after some time crystals which crystallized from dilute alcohol as fine needles which gave colourless solutions in the usual solvents, also in petroleum ether. The solution reacts acid. The melting-point is about 175° C. The substance has been named *mancopalinic* acid. Its analysis gave (mean of four analyses): C = 68·44; H = 8·37. Calculated for $C_{18}H_{12}O_2$: C = 68·57; H = 8·57. The molecular weight estimation gave, as a mean of five experiments, 137. Calculated for $C_8H_{12}O_2$ = 140. Its solution is dextro-rotatory, + 56°. The direct and indirect acid value is 397·6. The so-called saponification value, 394·8 cold, 397·6 hot. There is thus no difference between the saponification value and the acid value. One gramme of the acid absorbed 71·25 c.c. $\frac{n}{10}$ I = 0·9048 per cent iodine value. The potassium salt of mancopalinic acid is "salted" out when caustic potash in sticks is added to the dilute alkaline solution of the acid. It is washed and crystallized in alcohol. It forms needles containing 22·23 per cent K (calculated for $C_8H_{11}KO_2$ = 21·91 per cent K). The silver salt is precipitated from an alcoholic solution of the acid by adding silver nitrate drop by drop from its highly dilute solution in ammoniated alcohol. It contains 43·49 per cent silver (calculated for $C_8H_{11}AgO_2$ = 43·73). Mancopalinic acid is a monobasic acid. It contains neither a methyl group nor an aldehyde group nor a ketone group. The greater part of the ammonium carbonate extract acid is amorphous. This portion was neither precipitated by lead acetate nor by potash. It was dissolved in alcohol and precipitated from the alcoholic solution by lead acetate, the precipitate washed with alcohol, pressed therefrom, and treated with alcohol acidulated by sulphuric acid. The alcoholic solution filtered

from the separated lead sulphate was treated with water containing hydrochloric acid. The separated well-washed acid was dissolved in ether and the ethereal solution agitated with 1 per cent ammonium carbonate, the extract decomposed by hydrochloric acid washed and dried. The substance forms a white powder soluble in usual solvents. The solution is optically inactive. Melting-point, 100° to 105° C. This substance was termed mancopalenic acid. It gave on analysis: Found mean of four analyses: C = 67·83; H = 9·48. Calculated for $C_{18}H_{14}O_2$: C = 67·61; H = 9·86 per cent. Acid value: direct, 392; indirect, 394·8 to 397·6. Saponification value, cold and hot, 392 to 394·8. There is thus no difference between the acid value and the saponification value. Iodine value, 90·93 ($C_8H_{14}O_2I$ requires 89·44). One gramme of acid absorbed 71·6 c.c. n/10 I. It thus added one atom of iodine. One gramme of the acid absorbed 14 c.c. KHO = 0·2728 K; $C_8H_{14}O_2$ requires to form $C_8H_{13}KO_2$ = 27·46 per cent K. *Mancopalenic* acid is a monobasic acid. Sodium carbonate solution extracted 75 per cent of the resin. For the complete exhaustion of 1 kilo, 110 extractions were necessary. The crude acid is not salted out by caustic potash, but is split up by alcoholic lead acetate into a precipitable acid and a non-precipitable acid. The lead acetate precipitate was carefully washed with alcohol, pressed, and a portion treated with alcohol, acidulated by sulphuric acid, filtered from the lead sulphate, and the solution added to HCl water; the precipitated acid was then dissolved in ether, and extracted with sodium carbonate. The acid, which was termed *mancopalolic* acid, could not be obtained in crystals. It dissolves in the usual solvents, only slightly in petroleum ether, and is optically inactive. Its solution reacts strongly acid. Melting-point, 85° to 90° C. It gave on analysis: Found mean of four analyses: C = 70·35; H = 10·63 per cent. Calculated for $C_{10}H_{18}O_2$: C = 70·59; H = 10·59 per cent. Acid value: direct and indirect, 324·8 to 327·6. Saponification value: cold, 324·8 to 327·6; hot, 327·6 to 330·4. There is thus no difference between the acid and the saponification value. Iodine value, 74·54 ($C_{10}H_{18}O_2I$ requires 74·71). One atom of iodine was therefore added. One gramme of the acid required for saturation 11·6 c.c. $\frac{n}{2}$ KHO = 0·226; K = 22·61 per cent ($C_{10}H_{18}O_2$ requires for $C_{10}H_{17}KO_2$ 22·94 per cent K). Therefore α-mancopalolic acid is a monobasic acid. The solution, when filtered from the lead precipitate, should remain clear, and on the addition of excess of lead salt should give no further precipitate. When, therefore, a slight addition of alcoholic lead acetate gives no further precipitate, sulphuric acid is added, the lead sulphate filtered off, and the filtrate precipitated with water and the acid prepared as above. In this way β-mancopalolic acid was obtained in the amorphous condition like the α acid. Melting-point, 85° to 88° C. Its analysis gave: Found mean of four analyses: C = 70·39; H = 10·46. Calculated for $C_{10}H_{18}O_2$: C = 70·59;

H = 10·59 per cent. The β acid is thus an isomer of the α acid. Acid value: direct, 322·0 to 323·4; indirect, 327·6. Saponification value: cold, 327·6 to 330·4; hot, 330·4. There is thus no essential difference between the saponification value and the acid value. Iodine value, 74·54 ($C_{10}H_{18}O_2I$ requires 74·71). One gramme of the acid required for saturation 11·7 c.c. $\frac{n}{2}$ KHO = 0·2281 per cent; K = 22·81 per cent K ($C_{10}H_{18}O_2$ requires for $C_{10}H_{17}KO_2$ 22·94 K). *β-mancopalolic* acid is also a *monobasic* acid. Both acids are homologous with *mancopalenic* acid. The ethereal solution, after extraction by ammonium carbonate and sodium carbonate, cedes nothing further to caustic potash. It contains only the ethereal oil and the resene. The ether is expelled and the ethereal oil distilled with steam. The ethereal oil, dried over calcium chloride, is colourless, has a specific gravity of 0·840 and boils between 165° and 170° C. It is present to the extent of 6 per cent. From the residue left from the distillation the resene was prepared by repeated precipitation; it was soluble in chloral hydrate solution. The alcoholic solution reacted neutral. Melting-point, 80° to 85°. Present in the copal to extent of 12 per cent. Analysis gave: Found mean of three analyses: C = 83·43; H = 11·24. Calculated for $C_{20}H_{32}O$: C = 83·33; H = 11·11 per cent. The substance was termed mancopalresen.

The second sample of Manila copal examined by Tschirsch and Koch was one marked "M.C. hard shining". It did not agree in many points with the preceding. It came from Gorontalo in the Celebes. The melting-point was about 120°. It dissolved slightly in ether, likewise in alcohol, 80 per cent chloral hydrate acetone, benzol chloroform, slightly in carbon tetrachloride, but was absolutely insoluble in petroleum ether. Constants: Acid value: direct, 117·8; indirect, 156·8; saponification value: cold, 162·4 to 165·2; hot, 165·2 to 168; iodine value, 54·99. These values do not agree with the above soft copal. Dry distillation gave succinic acid along with formic and acetic acids. The copal ceded nothing to ammonium carbonate extraction whether of 1, 2·5, or 10 per cent strength. Sodium carbonate extracted two acids, in this case also constituting 80 per cent of the resin, which were separated by lead acetate.

TABLE LXXVI.—CONSTANTS OF α AND β MANCOPALOLIC ACID.

	α-Mancopalolic Acid.	β-Mancopalolic Acid.
Melting-point	88°-92° C.	86°-90° C.
Found mean of four analyses	C = 70·86	C = 70·71
" " " " "	H = 10·49	H = 10·49
Calculated for $C_{10}H_{18}O_2$	C = 70·59	—
" " "	H = 10·59	—
Acid value, direct	324·8-330·4	330·0-333·2
" " indirect	330·4	331·8-333·2
Saponification value, cold	324·8-330·4	330·4-336
" " hot	330·4	333·2
Iodine value	74·80	74·98

The ethereal oil was present in this sample to the extent of 5 per cent. Specific gravity was 0·840. Its boiling-point 165° to 170° C. Manila copal exhibits therefore the characteristics of a coniferous resin. The analysis shows it to be derived from a *Dammara*.

From the solution in ammonium carbonate two resin acids were obtained, one of which—mancopalinic acid—was crystalline, had a composition represented by the formula $C_8H_{12}O_2$ and a melting-point of 175°. The other, an amorphous acid—mancopalenic acid—had the formula $C_8H_{14}O_2$ and a melting-point of 100° to 105°. The solution of sodium carbonate dissolved two isomeric acids—*a*-mancopalolic acid, melting-point 90°, and *β*-mancopalolic acid, melting-point 88°, the formula of these acids being $C_{10}H_{18}O_2$.

After separation of these bodies the solution of caustic potash dissolved nothing from the ethereal solutions of the resins. The neutral substances left in the ethereal solution were a resinous body—mancopalresen, $C_{20}H_{32}O$, melting-point 80° to 85°—and a volatile oil which boiled at from 165° to 170°, and had a specific gravity of ·840. This oil oxidized and resinified on exposure to air, so that it was apparently a terpene.

The following figures represent approximately the composition of the two samples of Manila copal :—

TABLE LXXVI.—COMPOSITION OF HARD AND SOFT MANILA COPALS.

	Manila Soft Copal.	Manila Hard Copal.
Mancopalinic acid, Mancopalenic acid	4	0
a-Mancopalolic acid, β-Mancopalolic acid	75	80
Mancopalresene	12	12
Essential oil	6	5
Water	2	2
Succinic acid and impurities	1	1
	100	100

Bottler, in a description of Manila copal, says it is secreted by *Vateria Indica*, a dipterocarpus tree growing in the Philippine Isles. He is no doubt confusing a *Vateria* with a *Vatica*. It forms, he adds, large, cloudy, irregular, angular tears which often cohere into characteristically shaped stalactites—like masses of a yellow or brownish-yellow colour. The separate pieces have a conchoidal fracture ; the fracture is lustrous but the exterior is covered with a whitish-yellow earthy skin. The odour is aromatic and more decidedly so on rubbing. No characteristic taste is perceptible unless the copal is quite fresh, when it is slightly bitter. The powdered copal is white or yellowish-white. On heating Manila copal soon softens, begins to melt at 105° C., and is completely melted at 140°. When further heated it blisters, turns brown, and if then allowed to cool forms a hard,

scoriaceous mass. Its specific gravity is somewhat greater than that of kauri copal, being 1·069 at 15° C. It, too, belongs to the soft copals. It is known to the trade as hard yellow Manila copal.

Both kauri and Manila copals were treated by Bottler with various solvents, first when they had never been heated and after they had been melted, and also after they had been "roasted"—i.e. kept for some time at a high temperature, but one insufficient to fuse the copal. The unfused copals were coarsely powdered, and exposed to the air at a temperature of 15° to 20° C. for six weeks. The "roasted" copal was got by heating the coarsely powdered resin to between 40° and 50° C. for forty-eight hours. The molten copal was allowed to run through a sieve into a brass mortar, in which it was pulverized when cold, and then exposed to the air for a week.

FIG. 33.—Manila Copal—a typical lump broken to show conchoidal flint-like fracture. [Photographed specially for this treatise by Mr. C. Harrison, Borough Polytechnic, London, S.E.]

All the three samples were then finely powdered, and intimately mixed each with its own weight of powdered glass. The solvents tried were fourteen in number, viz. absolute alcohol, a mixture of equal volumes of absolute alcohol, and amyl alcohol boiling at 130° C., anhydrous ether, a mixture of ether and absolute alcohol, a solution of 1 part by weight of camphor in 12 of ether, chloroform, anhydrous acetone boiling at 57° C. and of a specific gravity 0·814, a mixture of equal volumes of carbon bisulphide, benzole, and rectified turpentine, rectified turpentine of specific gravity 0·87 alone, linseed oil, methyl alcohol of boiling-point 70° C., light tar oil, rosin oil (? spirit), and camphor oil. The results obtained here follow:—

A. With kauri copal } **(i) unmelted, (ii) after roasting, (iii) after fusing.**
B. With Manila copal }

A (i).—With the first two solvents the resin swelled up and dissolved almost completely, forming a clear solution. The mixture of ether and alcohol gives almost entire solution, but the resin only dissolved partly in the camphorated ether. In the chloroform it became gelatinous and scarcely dissolved at all in the cold, and although it dissolved to a turbid liquid on heating it all separated out again on cooling. A little dissolved in acetone, but the solution was not clear; the benzole mixture gelatinized it, and the oils had little effect. The copal scarcely dissolved in methyl alcohol, nor in tar oil, even on heating. Long heating with rosin oil (*sic*) had a little solvent action, but camphor oil could do nothing. The roasted resin was partly soluble in acetone, giving a cloudy solution which could be made bright by long digestion at 30° C. In turpentine or linseed oil it was scarcely soluble. Practically all the results were the same as with the copal which had not been heated.

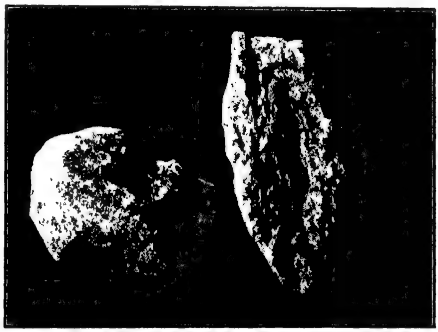


FIG. 34.—Kauri Copal—stalactitic. [Photographed specially for this treatise by Mr. C. Harrison, Borough Polytechnic.]

A (ii).—With the first two solvents the copal behaved like the unheated sample. In ether it dissolved partially. The alcohol and ether mixture dissolved it practically completely after long standing at 20° to 25° C. (68° to 77° F.). The camphoretted ether swelled it and dissolved more than of the unheated copal, but with chloroform there was no difference.

A (iii).—Here, again, practically the same results were achieved, although the resin was slightly more soluble in the various reagents than the roasted copal was.

The insolubility in turpentine and in linseed oil appears an insuperable bar to Manila copal ever becoming extensively used. Even if some of it dissolves after long heating, a lot of that separates out again on cooling.

B (i).—The copal dissolved nearly entirely in the alcohol. In the mixed alcohols and in the mixture of alcohol and ether it dis-

solved entirely on warming. Ether alone and camphorated ether both dissolved it almost completely. In chloroform or acetone it swells up and becomes gelatinous, and scarcely dissolves. In the benzole mixture it dissolves practically wholly, but the solution is turbid. Turpentine and linseed oil both failed to act on the resin, and methyl alcohol practically failed. Tar oil and rosin oil dissolved a little after long digestion. Camphor oil with the aid of heat dissolved more of the copal than it left, and after very prolonged heating dissolved it almost entirely.

B (ii).—The roasted copal was soluble in the first five solvents, and the solutions were almost colourless. In acetone it swelled up and dissolved slightly after long contact at 25° C. With the remaining solvents it behaved like the unheated resin.

B (iii).—Here, again, no differences of importance were noted. High temperature produced partial solution in turpentine, linseed oil, and in rosin oil, but the solubility only remained while the heating lasted. It must, however, be mentioned that the fused resin dissolved completely in the camphor oil to a clear solution.

The above researches show, first, that these copals can serve for the making of spirit varnishes, and also what are the best solvents, viz. the absolute alcohol, the mixture of equal volumes of absolute alcohol and amyl alcohol, and the mixture of ether and absolute alcohol. For the roasted and fused copals, camphorated ether will also serve. In the experiments about 5 parts of solvent were used to 1 of copal, and the consistency of the solution could be increased by evaporating off some of the solvent. An oil varnish can, however, be made by stirring into 8 parts by weight of the copal in a fused condition 25 parts of hot linseed oil. The varnish is then boiled with 1 part of manganese borate to every 400 of linseed oil, and finally 20 parts of turpentine are added, a little at a time. The oil used should be first bleached with sulphate of lead. The finished varnish may be dyed with aniline colours, dragon's blood, etc., and will give shining and durable coats on paper, glass, wood, and stone (Bottler).

Mastic.—Mastic was well known to the ancient philosophers. Galen (A.D. 131-210), physician to Marcus Aurelius, the elder Pliny (A.D. 23-79), and Dioscorides, Patriarch of Alexandria (died A.D. 454), mention it in their writings. *Origin.*—Mastic of commerce is secreted by the *Pistacia lentiscus anacardiaceæ*, a shrubby tree indigenous to the Levant and the Greek Archipelago, but cultivated chiefly in the island of Chios. Each tree yields annually ten to twelve pounds. The greater part of the annual production is sent as tribute to the Turkish Government and the rest sent to market. The *Pistacia lentiscus*, the source of mastic, is found all over the coasts of Southern Europe and Northern Africa; but mastic is obtained from the island of Chios alone, as it has been from very ancient times. There a broad-leaved variety of the plant is culti-

vated in the vicinity of about twenty villages—known as Masticho-chora, or mastic villages—on account of the high yield and excellent quality of the mastic it produces. This form of mastic, termed "Schinas" locally, was known to Duhamel; and a commoner variety, which, however, does not produce a suitable mastic, is also found in Chios. According to Heckel, Afghanistan and Beluchistan furnish the London market with an inferior quality of mastic, obtained from *Pistacia khinjuk* stocks and *Pistacia cabulica* stocks, the former plant being indigenous throughout those countries at altitudes of 4000 to 8000 feet. This latter resin is used as a substitute for true mastic, both locally and in Scinde and Persia, and is known under the names Roomie-mustakie, Koondur-Roomie (among the Arabs), Kundiron-Sakiz-sheren (by the Persians), and also as Aluk-vol-unbat. According to information received, the resin is called Kundiron or Sakiz-sheren (sweet mastic) among the Persians, in order to distinguish it from olibanum, known as Kundir or Sakiz-Tulkh (bitter mastic), as well as from true or Turkish mastic (Kundir-Roomie or Sakiz-Roomie). The product from *Pistacia cabulica* stocks is called by the following native designations in the countries of origin: Mustaka-arab, Uluk-bagadame, Aulug-dagdadie (by the Arabs), Roomie-mustakie, Koondur-roomie (by the Hindus), Kinneh, Kinnoli (by the Persians), Sakiz-Khinjuk (by the Afghans), Shat-i-Kundiroo (by the Sikhs), and Aluk-ool-unbat (by the Rohillas).

Mastic exudes spontaneously from the plant in small quantities and hardens on the twigs in the form of drops, the trees having to be incised to obtain larger supplies. A number of long cuts, extending from the base of the trunk to the level of the branches, are made in the bark, and from these the resin exudes, some of it hardening at the cuts, and the rest falling to the ground and settling in the form of grains. Formerly the practice was to wet the soil round the trees and ram it firm in order to prevent contamination of the resin by particles of earth, but at present a cleaner product is obtained by laying stone flags underneath the trees.

Mastic from P. mutica.—In Watt's "Dictionary of Indian Products" *Pistacia R. mutica*, Fisch and Mey, is treated as the Asiatic representative of *P. terebinthinus*, the plant which yields the Chian or Cyprus turpentine, but it is now regarded as a distinct species. It occurs commonly in Beluchistan. The resin resembles that of *P. lentiscus* and is used in the East as a substitute for that substance. It bears the same vernacular names and is regarded as identical with mastic from *Pistacia vera* (the Pistachio nut-tree). A small tree forming forests at 3000 feet in Syria, Damascus, Mesopotamia, Terek, the Badghis and Khorassan yields, besides the edible nut, a resin similar to mastic setting hard enough to collect. The best quality is that taken off the twigs, and is packed in baskets lined with paper or cotton cloth. The grains collected from the stone flags form a second quality, whilst a third, less pure grade, is picked

from the interstices of the flags. The collecting period extends over two months, and each tree yields 9 to 10 lb. of mastic.

Unger has made exhaustive researches into the origin and occurrence of mastic in the tissues of *Pistacia lentiscus*. It appears that the secretion is formed in special resin ducts occurring in gaps left by the dense, undulating bast cells, and forming intercellular cavities free from any trace of residues of cellular tissue. Even in very young stems these resin ducts can be recognized as broad, sharply defined cavities filled with resinous sap free from residues of tissue. Unger therefore concludes that the resin of *Pistacia lentiscus* is not formed by chemical metamorphosis due to the wounding of the cells, but is produced in the cells themselves and secreted in the resin ducts. By the scaling off of the bark the

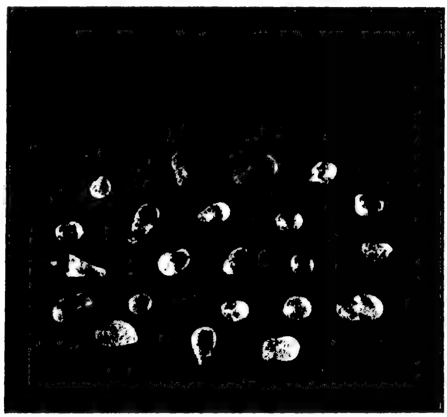


FIG. 35.—Mastic. [Photographed specially from nature for this treatise by Mr. C. Harrison, Borough Polytechnic.]

ducts are brought so near to the surface that a very slight wounding is sufficient to a flow of resin. Mastic tears are rounded to elongated in shape, measuring one-fifth to four-fifths of an inch across, with a yellowish or greenish colour (attributed to chlorophyll by Fluckiger), and a peculiar smell and taste resembling those of swede turnips. The smell of mastic also recalls that of Galbanum resin. Individual tears are golden yellow, partially tinged a peach-blossom red. The tears are more or less cloudy in appearance, and dusty on the surface. This characteristic is not the result of the mutual attrition of the grains, but arises from the considerable shrinkage of the outer stratum of the grains giving rise to the formation of faceted cracks. In point of hardness mastic comes midway between dammar and sandarach. Pfaff gives the specific gravity as 1·04, Schroetter and Brisson as 1·07. The surface of fracture is

conchoidal and with a glassy lustre when fresh. When chewed, mastic forms a pasty mass, whereas all other resins—including especially the sandarach, with which it is often adulterated—crumble to powder under this treatment.

According to Johnstone, mastic melts at 100° C., and Schroetter states that it softens at 80° C., and melts with incipient decomposition at 105° to 120° C. The constituent substances include a free substance (mastic acid or a resin with an acid reaction) soluble in alcohol, a resinous compound (masticine or B-resin) insoluble in alcohol, but soluble in ether and oil of turpentine, and small quantities of a volatile oil in freshly collected resin. Johnstone gives the formula of mastic acid as $C_{40}H_{64}O$, masticine $C_{40}H_{62}O$, and the relative proportions are about 80 to 91 per cent of the former, the rest consisting of masticine exclusively. In the East mastic is largely consumed as a chewing-gum, for which purpose, however, only the very finest quality—the so-called Filiskari or seraglio resin—is employed, which is therefore never available for other uses.

Tschirsch and Reuter examined the best Chios mastic on the market. *Solubility.*—It was *insoluble* in water, *partially soluble* in spirits of turpentine, carbon disulphide, methyl and ethyl alcohol two-thirds, *almost completely soluble* in petroleum ether, acetone, amyl alcohol, *completely* soluble in acetic ether, chloroform, ether, xylene, benzene, toluene, chloral hydrate. The solution reacts acid. *Constants.*—Acid value: direct mean, 59·2; indirect mean, 58·9. Saponification value: cold, 81·8; hot, 83·0. The examination was conducted in the usual way, viz. by extracting the ethereal solution with 1 per cent ammonium carbonate, 1 per cent soda solution, and 1 per cent potash.

a Masticinic Acid, $C_{23}H_{36}O_4$.—It required twenty extractions with ammonium carbonate to exhaust the solution. The acid precipitated by hydrochloric acid (4 per cent of the mastic) was soft and amorphous and could not be crystallized. It was therefore precipitated by an alcoholic solution of lead acetate. One portion was precipitated, the other remained in solution and did not fall out on the addition of more acetate of lead. The lead acetate precipitate, after careful washing, was treated with alcohol acidified with sulphuric acid and filtered. The sulphuric acid was removed from the filtrate by white lead and water acidified by HCl added to the filtrate. The precipitated resin acids formed after drying a soft amorphous powder, very refractory to crystallize in any solvents, soluble in the usual solvents and in petroleum ether. Melting-point, 90° to 91° C. Optically inactive. Acid value: direct mean, 141·07; indirect, 140·39. Analysis—mean of three: C = 73·17; H = 9·2. Calculated for $C_{23}H_{36}O_4$: C = 73·4; H = 9·57. The acid was termed *a* masticinic. The monopotassium salt $C_{23}H_{35}O_4$ K requires 9·42 per cent K. The potassium content on titration gave 8·96 per cent K. The salt is therefore monobasic.

β Masticinic Acid.—To the filtrate from the lead acetate precipi-

tate, weak nitric acid was added. The precipitate was well washed and tested if crystallizable with various solvents. It did not crystallize. Melting-point, 89° to 90·5° C. It dissolves in the usual resin solvents, including petroleum ether, and is optically inactive. Acid value: direct mean, 131·2; indirect mean, 132·6. Analysis of the substance dried at 80° C.—mean of two: C = 73·34; H = 9·2. Calculated for $C_{23}H_{36}O_4$: C = 73·4; H = 9·57. The acid was termed β masticinic acid; it is isomeric with α masticinic acid. The potassium content by titration was 8·37. $C_{23}H_{35}KO_4$ requires 9·42 per cent K. The acid is thus monobasic.

Masticolic Acid.—By extraction with 1 per cent soda solution about 380 grammes of crude acid were obtained. This acid was separated by hot alcoholic solution of lead acetate. The lead acetate precipitate after careful washing was treated with alcohol acidulated by H_2SO_4, the lead sulphate filtered, and the free sulphuric acid removed from the filtrate by white lead. The filtrate was then run into water acidulated by HCl and the precipitate well washed. It was dissolved in alcohol to crystallize. It soon yielded crystals like long colourless needles. Melting-point, 201° C. Readily soluble in petroleum ether, ether acetone, acetic ether, chloroform, benzene, toluene, xylene, spirits of turpentine, and 80 per cent chloral hydrate; with more difficulty in ethyl alcohol, amyl alcohol, methyl alcohol; insoluble in water. Analysis of substance dried at 100° C.—mean of three: C = 73·34; H = 9·69 per cent. Calculated for $C_{23}H_{36}O_4$; C = 73·4; H = 9·57. Molecular estimation by the boiling-point method gave—353, 330, 398, 382, 398; mean 372. Calculated for $C_{23}H_{36}O_4$, 376. The acid was termed masticolic acid; it is isomeric with α and β masticinic acid. It only amounts to 0·5 per cent of the mastic. Acid value: direct mean, 132·5; indirect, 131·7. The formula $C_{23}H_{35}KO_4$ requires 9·42 per cent K. The potassium content by titration was 8·46 per cent K. The silver salt prepared by precipitation with silver nitrate with the addition of a few drops of ammonia gave 21·9 per cent and 21·6 per cent Ag. For $C_{23}H_{35}AgO_4$ 22·36 per cent Ag is required. The salt is thus monobasic.

α Masticonic Acid.—Only a small proportion crystallized from the alcoholic solution; the remainder was amorphous and remained amorphous in all crystallization media. It was dissolved in alcohol, treated with bone-black and filtered, and after filtration precipitated by HCl. This acid was soluble in the same solvents as the preceding. It intumesced at 95° C. and melted at 96° to 96·5° C. Acid value: direct mean, 107·55; indirect, 106·05. Analysis of substance dried over sulphuric acid—mean of three: C = 77·99; H = 9·25. Calculated for $C_{32}H_{48}O_4$: C = 77·42 per cent; H = 9·68. The acid was termed α masticonic. It formed 20 per cent of the mastic. The potassium salt calculated by titration gave 6·99 per cent K. For $C_{32}H_{47}KO_4$ 7·39 per cent K is required. *β Masticonic Acid*—the filtrate from the lead precipitate—was treated with bone-black and then digested with water acidulated by HNO_3; the precipitated acid

was well washed and dried. It could not be broken up further. Melting-point, 91° to 92° C. Optically inactive and soluble in the same solvents as the preceding. Analysis of the substance dried at 80° C. —mean of three: C = 76·99; H = 9·87. Calculated for $C_{32}H_{48}O_4$: C = 77·42; H = 9·68 per cent. Acid value: direct mean, 103·2; indirect, 103·1. The potassium salt gave by titration 6·81 per cent K. For $C_{32}H_{47}KO_2$ 7·3 per cent K is required. This acid, β masticonic acid, is also monobasic. It forms 18 per cent of mastic. The ether solution after treatment with ammonium carbonate and soda ceded nothing further to potassium hydrate. It was freed from potassium by washing with water, the ether driven off, and the residue steam distilled. The ethereal oil separated in the usual way was pale yellow and somewhat camphoraceous. It formed 2 per cent of the mastic. The residue in the flask from the steam distillation of the oil tasted very bitter. The bitter principle could not be isolated in a pure form. It gave the usual reactions with iron chloride, lead acetate, and tannin. One part of the resinous body left in the flask was dissolved in alcohol. The solution was precipitated by acidulated water and the precipitation several times repeated. The substance is then white amorphous, incapable of being crystallized from any solvent soluble in all resin solvents. Melting-point, 74° to 75° C. Analysis of substance dried over H_2SO_4—mean of three: C = 77·42; H = 10·07. Calculated for $C_{35}H_{56}O_4$: C = 77·78 per cent; H = 10·37. The substance, a mastico-resene, is optically inactive. It forms 31 per cent of mastic. The insoluble portion, β mastico-resene, was incapable of being brought into a pure enough form for analysis. It remains in paste form after repeated precipitation from the ethereal solution. It is insoluble in ethyl and methyl alcohol. It dissolves in the usual resin solvents. It forms 20 per cent of mastic.

TABLE LXXVIII.—COMPOSITION OF MASTIC (TSCHIRSCH).

I. Free Resin Acids :—	
(*a*) Soluble in 1 per cent ammonium carbonate :—	
α Masticinic acid precipitable by lead }	4·0
β Masticinic acid not precipitable by lead } Isomeric $C_{23}H_{36}O_4$	
(*b*) Soluble in soda :—	
Masticolic acid crystalline $C_{23}H_{36}O_4$ } precipitable by lead	0·5
α Masticonic acid amorphous $C_{32}H_{48}O_4$ } precipitable by lead	20·0
β Masticonic acid not precipitable by lead $C_{32}H_{48}O_4$	18·0
II. Resenes :—	
α Mastico-resene $C_{35}H_{56}O_4$ soluble in alcohol	30·0
β Mastico-resene insoluble in alcohol (masticin)	20·0
III. Ethereal Oil	2·0
Bitter principle, impurities, etc.	5·5
	100·00

Mastic is a resene-resin. Johnstone's *a* resin or mastic acid contains the above five resin acids, and the mastico-resene soluble in alcohol. His β resin or masticin is an impure mastico-resene.

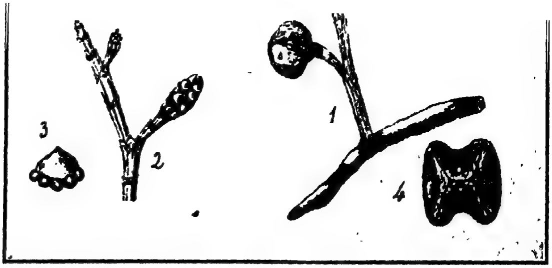


FIG. 36.—*Thuya Articulata*, Desf [*Callitris Quadrivalvis*, Rich]. 1, flowering branch and fruit; 2, a male flower greatly enlarged; 3, stamen, dorsal view; 4, fruit viewed from above.

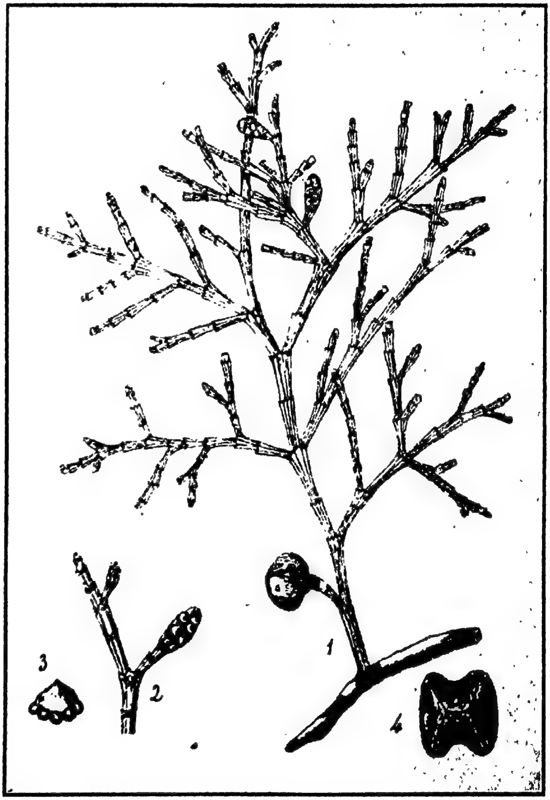
Mogadore Sandarach, also, but erroneously, known as gum juniper, is a resin which exudes naturally from the bark of one of the North-west African conifers, viz. the *Thuya articulata*, Desf, a small cypress tree which thrives more especially on the southern watersheds of the Atlas chain of mountains. The yield is increased by making incisions on the trunk near the bottom, analogous to those used in obtaining mastic. The oleo-resin as it exudes has obviously high refractive power, and much

Dust.—The surface of the tears appears to be covered more or less with powder, but this is not due to the mutual attrition of the fragments one against another, but to the unequal contraction of the resin in drying, resulting in a mass of fissures that form, as in the case of several kinds of copal, facets that gradually separate from the mass and constitute the powder of many authors. In support of this view it has been pointed out that resins of the sandarach class are nearly white on the trees after they have exuded some time, showing that the appearance is brought about by exposure to the weather.

Solubility.—Mogadore sandarach is very soluble in ether, which appears to be its best solvent. It dissolves in methylated spirit 64° O.P. and also in amyl alcohol and in acetone. It only dissolves partially in spirits of turpentine, benzene, toluene and chloroform, and only a very small amount dissolves in petroleum ether.

Adulteration.—It rather serves for the adulteration of other resins than being itself adulterated. It is better, however, to make sure that it has not been sophisticated by German sandarach gum juniper, a resin which is exuded exclusively by old juniper bushes. On heating the "gum" juniper gives off a characteristic odour by which it is recognized. Rosin would increase the acid value and the solubility in turps, petroleum ether, and other individual solvents.

Sandarach.—There are two kinds of sandarach on the London market: (1) Mogadore sandarach; (2) Australian sandarach. The latter is of comparatively recent introduction.



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resembles ordinary freshly exuded turpentine oleo-resin in general appearance, also both in taste and in smell. In this condition it is very irritating to a cut or wound. The tree is reproduced from seeds, and the seed beds ought to be sown with very fresh seed. Algeria and Morocco are the two regions where the *Thuya* thrives best; and it is from there, more especially from Morocco, that the African sandarach used in Europe to such a large extent in spirit varnish-making comes. African sandarach is shipped to this country from Mogadore. Hence the term Mogadore sandarach. The best quality of sandarach is in very pale yellow, almost colourless tears covered with a fine whitish dust with a vitreous fracture, and transparent when the interior of the pieces is examined. But there is a second quality of sandarach termed *common* sandarach which is met with in rounded or elongated tears of a dark yellow or saffron colour, opaque, and highly impure.

Physical Properties.—Mogadore sandarach is hard but brittle. The slightly conchoidal arched fracture has a glistening lustre when fresh. It is easily crushed under the teeth, becoming reduced to a finer and finer powder, the particles of which do not agglutinate together as in the case of mastic. It has a faint smell of turpentine and a slightly bitter balsamic taste. It commences to soften at 100° C. (212° F.), melts at 135° C. (275° F.), catching fire and at the same time emitting a characteristic pleasant smell. Its density is 1·092 according to Brisson, 1·05 according to Pfaff, and 1·066 according to Fluckiger. Old samples have a mealy appearance, but this is merely superficial, and has been accounted for as follows:—

Dust.—The surface of the tears appears to be covered more or less with powder, but this is not due to the mutual attrition of the fragments one against another, but to the unequal contraction of the resin in drying, resulting in a mass of fissures that form, as in the case of several kinds of copal, facets that gradually separate from the mass and constitute the powder of many authors. In support of this view it has been pointed out that resins of the sandarach class are nearly white on the trees after they have exuded some time, showing that the appearance is brought about by exposure to the weather.

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Analysis.—Tschirsch and Balzer examined Mogadore sandarach. Later on Tschirsch in conjunction with Wolff made a fresh examination, using modified methods. The following is his mode of procedure and the results of the first examination. Dry distillation yielded acetic acid and a substance rich in a sort of borneol. Also a substance which gave some of the reactions of succinic acid. The examination was made on a pure resin prepared thus: The sandarach was dissolved in alcohol and precipitated by water. The bitter principle remained in solution and a little ethereal oil, 0·5 per cent of the sandarach. The pure resin separated and by repeated precipitation was freed from both these bodies. On treating the sandarach with 96 per cent alcohol it completely dissolved except a small amount of plant debris and some wind-borne bassorin granules. The sandaricin insoluble in alcohol could not be isolated. The purified resin like crude sandarach dissolved in alcohol, ether, amyl alcohol, acetone, and ethereal oils and dilute alkalis; very slightly in benzene, toluene, xylene, chloroform, and petroleum ether; also in concentrated alkalis. Sulphuric acid dissolved it cherry red. The alcoholic solution reacted acid. The bitter principle left in the solution from which the purified resin is precipitated can on evaporation of the solution and extraction of the residue with ether, or by precipitation with lead acetate, be obtained as a yellow powder, but not by any means pure enough for analysis. It is not glycosidic in character. A test to saponify the resin with potash or sulphuric acid failed. It was scarcely affected by these reagents; it therefore contains no ester. The method of procedure followed was not by extraction but by working direct on the pure resin; it was dissolved in 1 per cent potash solution and stick potash added until no precipitate occurred. A thick white precipitate was produced which was dissolved in water, HCl added, and the *sandaracolic* acid liberated. The stick potash solution from which the precipitate was separated yielded on acidulation with hydrochloric acid a second acid, *callitrolic* acid. The sandaracolic acid separated from the potassium resin compound —the resin soap—was soluble in alcohol ether, acetone, dilute potash, in concentrated sulphuric acid with a red colour; insoluble in benzene, toluene, petroleum ether, chloroform, and ammonia. It crystallized with difficulty. It is best crystallized by precipitation with lead acetate and decomposing the lead compound. Melting-point, 140° C. Analysis—mean of three: C = 75·23; H = 9·25. Calculated for $C_{45}H_{66}O_7$: C = 75·21; H = 9·19. By solution in normal alkali and back titration 5·6 K was consumed. $C_{45}H_{66}O_7$ requires for the monopotassium salt 5·43 per cent K. By the addition of ammonia to render the alcoholic solution of sandaracolic acid alkaline, the silver salt gradually falls out on adding silver nitrate. The silver determination gave 12·79 and 12·84. For Ag $C_{45}H_{65}AgO_7$ 13·07 Ag is required. When an alcoholic solution of sandaracolic acid is mixed with freshly precipitated cupric hydrate, evaporated to dryness on the water-bath, and the residue taken by

a mixture of alcohol and ether, a copper salt is dissolved which, on evaporation of the alcohol ether, remains as a green powder, cupric abietinate soluble in carbon disulphide. The copper in this compound is masked. It is not detected by ammonia, nor by potash, nor by sulphuretted hydrogen. The salt contains water. Three estimations gave 1·5, 1·6, 1·9 per cent H_2O. It gave a copper content of 0·94, 1·10, 1 per cent. By precipitating a solution of the potassium salt of sandaracolic acid a basic copper salt was obtained containing 11 per cent Cu. If sandaracolic acid be acetylated with acetic anhydride in a tube at 175° C. a coloured acetyl derivative is obtained which does not dissolve in alkalis, nor even in chloroform, and only slowly in potash. Analysis—mean of two: C = 74·16; H = 9·07 per cent. Calculated for $C_{45}H_{65}O_7$: C = 74·21; H = 8·95 per cent. Benzoylation yields with sandaracolic acid a benzoyl derivative which dissolves in most of the solvents for the acid, not in acetic acid, nor even in chloroform. Analysis—mean of two: C = 75·63; H = 8·18. Calculated for $C_{45}H_{65}O_7$, C_6H_5CO: C = 75·91; H = 8·52 per cent. Sandaracolic acid, therefore, contains a hydroxyl group and can be represented as $C_{45}H_{65}O_6OH$, or $C_{44}H_{64}O_4$ OH·COOH. It is thus either a resinol or a resinol acid. Distilled with zinc dust 1 : 5 at about 180, 35 per cent of a dark fluid was obtained which dissolved in ether, and freed from phenols by caustic soda on evaporation of the ether gave a strongly fluorescent residue which was heated with metallic sodium under a reflux condenser and then fractionated. The first four fractions, 80° to 110°, 110° to 115°, 115° to 150°, 150° to 175°, were colourless; the fifth, 175° to 200°, was yellowish. The first fraction contained benzol, identified by the formation of nitrobenzol, anilin, and isonitrile; the second, toulene; it gave oxybenzoic acid. Melting-point, 121° C. From the third and fourth fraction by oxidation a substance smelling of thymol was obtained. The fifth fraction gave a strong reaction with nitric acid. It thus also contained aromatic hydrocarbides. Nitric acid yields with sandaracolic acid both picric and oxalic acid, identified by their reactions, an oxidation product free from nitrogen oxysandaracolic acid which, in immersing the reaction mixture in water, falls out as a yellow body. Analysis—mean of two: C = 65·12; H = 5·84. Calculated for $C_{40}H_{42}O_{13}$: C = 65·75; H = 5·75 per cent. The various attempts made to discover the action of fused potash on sandaracolic acid and abietinic acid all failed, however the experiments were varied. Oxidation with permanganate gave no result. Only chromic acid mixture gave a new body, melting-point 200° C., insoluble in alcohol, which can be purified by solution in alcoholic potash and precipitation by HCl. With zinc dust sandaracolic acid is reduced in acetic acid solution. It is sulphonated by sulphuric acid. The dark brown sulphonated product dissolves in alcohol ether, acetone, glacial acetic acid, chloroform; also in toluene and benzene; insoluble in potash solution. There is separated from the resin solution from which the potassium salt of sandaracolic acid was separated by

stick potash, on the addition of HCl, a yellowish precipitate, difficult to purify even after repeated precipitation from its alcohol solution by water and re-crystallization from strong alcohol, tubular, colourless crystals separate, melting-point 248° C., which dissolve in alcohol, ether, acetone, glacial acetic acid, dilute potassium carbonate, and concentrated potash (differentiation from sandaracolic acid), insoluble, however, in benzene, toluene, chloroform, and petroleum ether. This acid, callitrolic acid, gave on analysis—mean of two: C = 77·60; H = 8·46. Calculated for $C_{62}H_{80}O_8$: C = 78·15; H = 8·40. The molecular weight estimation gave 921, the formula $C_{62}H_{80}O_8$ requires 952. Heated in tube for eight hours with acetic anhydride at 175°, callitrolic acid yields an acetyl derivative soluble in chloroform, benzene, toluene, glacial acetic acid, and potash solution. Analysis—mean of two: C = 77·67; H = 8·38. Calculated for $C_{62}H_{79}O_8CH_3CO$: C = 77·26; H = 8·25. A hydroxyl has here also to be added to the formula. By digesting the alcoholic solution of callitrolic acid with freshly precipitated cupric hydrate, a salt is obtained in the manner already described, soluble in alcohol and ether, which crystallizes from the alcohol in green plates. Melting-point, 185° C. Two estimations gave Cu 5·73 and 6 per cent Cu content. The formula $C_{62}H_{78}O_8$ requires 6·21 per cent Cu. Callitrolic acid is thus dibasic.

The earliest investigation of sandarach was made as far back as 1839 by Johnstone, but his results were not very reliable. Beyond determining such constants as specific gravity, acidity, etc., nothing was done to ascertain the chemical composition of sandarach until 1896, when Tschirsch and Balzer determined the composition of sandarach as sandaraolic acid 85 per cent, callitrolic acid 10 per cent, ethereal oil and bitter principle 2·84 per cent, water 0·5 per cent, ash 0·1 per cent, impurities 1·5 per cent. The composition was ascertained by saponifying the resin with caustic potash, separating out the acids by fractionation and treatment with acid, as just described—a process that is open to the objection that the saponification may cause some changes in the composition of the acid bodies present, so that these are not ultimately obtained in the same condition as they are present in the original resin.

Henry recently examined sandarach and incidentally reviewed the work of former investigators, and finds that they have made numerous arithmetical errors in calculating the results of their experiments, which renders their statements as to the composition of the compounds they separated from the resin of no value. Henry's results are as follows: Sandarach contains a mixture of resin acids and volatile hydrocarbons. To separate the latter Henry adds alcoholic potash to the alcoholic solution of sandarach, removes the alcohol by heating, and dissolves the residue in water by agitating the solution with ether. He extracts therefrom two hydrocarbides, one consisting of a diterpene, boiling at from 260° to 280° C., specific gravity 0·9386, having the formula $C_{20}H_{32}$, and a pineneter-

pene having the gravity 0·858, boiling from 152° to 159° C., and having the formula $C_{10}H_{16}$. There are two resin acids in sandarach, one is a crystalline pimaric acid, separated from the alkaline solution of the resin, repeated precipitation by 20 per cent potash having the formula $C_{20}H_{30}O_2$, melting at 171° C.; soluble in alcohol ether, chloroform, and acetone, but insoluble in water and petroleum. The molecular weight appears to be 302. Henry made and examined many compounds of this acid, which is the chief constituent of the resin. It yielded on oxidation probably trimellitic acid, no oxalic acid or acetic acid. The other acid is callitrolic acid, having the formula $C_{30}H_{48}O_5$. Henry does not give the proportions of these constituents present in the resin.

To clear up the difference between Balzer's results and those of Henry, Tschirsch and Wolff made a new examination of sandarach, using the methods adopted for the examination of coniferous resins which were not known when sandarach was first examined by Tschirsch. The sample examined was completely soluble in alcohol, acetone, amyl alcohol, turpentine oil, petroleum ether, benzene, toluene, xylene, and carbon disulphide. It was completely soluble in 3 parts ether. On diluting with ether much white resin was precipitated. Sandarach dissolves clear in ether if dilute acetic acid or dilute HCl is added. Acid value: direct, 138·6 to 140; indirect, 141·4 to 142·8. Saponification value: cold, after twenty-four hours 162·4, forty-eight hours 161·0, seventy-two hours 163·8, ninety-six hours 165·2. Saponification value: hot, one hour 166·6, two hours 163·8, three hours 168·0, four hours 166·6. Dry distillation gave neither succinic acid nor retene nor hydroretene.

Ammonium carbonate extracted about 2·3 per cent of the sandarach. The resin acids were precipitable by lead or by strong potash. The free acid dissolved in the usual solvents, but not in petroleum ether, chloroform, and benzene. It was termed *sandaracinic* acid. It is amorphous, it is coloured red at 175° C. Melting-point, 186° to 188° with decomposition. It contains no methoxyl, is optically inactive. Analysis—mean of two: C = 76·09; H = 10·17. Calculated for $C_{22}H_{34}O_3$: C = 76·30; H = 9·83 per cent. Potassium salt titration gave 10·32 per cent K. Calculated for $C_{22}H_{33}KO_3$ = 10·16 per cent K. Acid value: direct, 162·4; indirect, 162·4 to 163·8. Saponification value: cold, twenty-four hours 173·6, forty-eight hours 175. Saponification value: hot, one hour 173·6, two hours 176·4. Extraction with soda yielded an acid mixture which could not be separated by potash, only by lead acetate, into two portions. The addition of lead acetate to the extract was repeated until the crystalline acid re-dissolved in the excess of lead acetate, from which it was then precipitated by other acids. The acid precipitated by lead; the sandaracinolic acid dissolves in the usual solvents; not in chloroform, benzene, or petroleum ether. Melting-point cannot be determined. The substance decomposed about 265° to 275° C. Analysis—mean of three: C = 77·72; H =

9·93. Calculated for $C_{24}H_{36}O_3$: C = 77·42 ; H = 9·68 per cent. Potassium salt by titration gave 10·06 K. Calculated for $C_{24}H_{35}KO_3$ = 9·51 per cent K. Acid value : direct, 159·04 to 161·28 ; indirect, 160·16. Saponification value: cold, twenty-four hours 160·16, forty-eight hours 161·28. Saponification value: hot, one hour 164·64, two hours 170·24, three hours 172·48. On hot saponification the solution turns red ; methoxyl is absent. It can be acetylated. The acetylated product was not obtained pure enough for analysis. Boiled with alcoholic potash hydrolysis occurred, then a slight partial decomposition. The acid not precipitated by excess of lead acetate ; the sandaraco pimaric acid was after purification by ethyl-methyl alcohol obtained as long crystalline needles 1 to 2 cm. long which dissolved in the usual solvents and also in petroleum ether. Melting-point, 170° C. From dilute alcohol the acid crystallizes in rosettes.

TABLE LXXIX.—ULTIMATE ANALYSIS OF SANDARACINIC ACID.

Analysis—mean of three : C = 79·08 ; H = 10·17.
Calculated for $C_{19}H_{28}O_2$: C = 79·16 ; H = 9·73.
" $C_{20}H_{30}O_2$: C = 79·47 ; H = 9·94.
" $C_{20}H_{32}O_2$: C = 78·94 ; H = 10·35.
The potassium salt gave 11 per cent.
$C_{19}H_{27}KO_2$ requires 11·96 per cent K.
$C_{20}H_{29}KO_2$ " 11·47 "
$C_{20}H_{31}KO_2$ " 11·40 "
The silver salt gave 26·69 per cent Ag.
$C_{19}H_{27}AgO_2$ requires 27·32 "
$C_{20}H_{29}AgO_2$ " 26·39 "
$C_{20}H_{31}AgO_2$ " 26·26 "

The average iodine value = 139. Acid value : direct, 186·6 ; indirect, 186·6. Saponification value : cold, twenty-four hours 188·83, forty-eight hours 192·27, seventy-two hours 194·0. Saponification value : hot, one hour 194·0, two hours 196·8. The acid contains no methoxyl and cannot be acetylated. It is identical with the i-pimaric acid isolated by Henry.

By extracting the last extracted fluid by energetic shaking with carbonate of soda solution a sodium compound was isolated which crystallized from both water and benzol, as white mother-of-pearl shining crystalline plates. The melting-point of air-dried substance is 83° to 85° C. It dissolves in solvents to a colourless solution, is odourless and tasteless, and does not reduce Fehling's solution. When stored some time in a dessicator the substance gives off a formaldehyde-like odour, takes a bitter taste, becomes pasty, and reduces Fehling's solution and silver nitrate. With water it then gives an incomplete turbid solution which clarifies on the addition of a little soda, yet remains coloured a deep yellow by further addition of dilute soda. Several tests of the salts obtained by precipitation show no agreement in the elementary analysis. Thus one precipitate gave mean of two : C = 71·37 ; H = 9·47. Another precipitate stored several weeks

over P_2O_5 gave mean of two: C = 76·45; H = 9·34. The free acid showed on long storage as the salt did a smell and a bitter taste, and also reduced Fehling's solution when dissolved in caustic soda. Whether any, and if so, what relationship this free acid bears to Henry's anhydride of callitrolic acid, from which he separated from its solution in absolute alcohol by the addition of dilute sodium alcoholate and the decomposition of the unisolated precipitate a crystalline sodium salt, cannot yet be exactly determined.

The substance with the bitter taste remains on precipitating the acid with water acidulated by HCl or H_2SO_4, and can, by evaporating the residue and neutralizing the filtrate, be extracted by alcohol. On driving off the alcohol a brown mass remains with an intensive bitter taste similar to that of sandarach. Further characteristic reactions could not be tested with the small amount found. Here for the first time is shown an example of a tasteless resin becoming bitter which throws much light on the auto-oxidation of other resin acids. The resene sandaracoresene is soluble in alcohol ether, acetone, benzene; insoluble in petroleum ether and alkalis. It melts at 57° C. It forms about 3·3 per cent of the resin. Analysis—mean of two: C = 79·59; H = 10·71. Calculated for $C_{22}H_{36}O_2$: C = 79·52; H = 10·84 per cent. The bitter principle found in the extracts was unattainable. The ethereal oil passed over between 152° and 159° C.; it forms about 1·3 per cent of the sandarach. Researches up to the present time have established that Henry's i-pimaric acid is identical with sandaraco-pimaric acid, the presence of a resene, ethereal oil, and a bitter principle, also a substance which gives a crystalline sodium compound which in three tests of sandarachs from different sources was also isolated. The more intimate properties of the amorphous acids, the preliminary extraction and subsequently crystallization of callitrolic acid require further examination.

Australian Sandarach.—This resin has now been on the London market for nearly two decades. An article in the "New South Wales Agricultural Journal" by Maiden, which the writer introduced to a London journal devoted to the oil and colour trade, first brought this colonial resin prominently before spirit varnish-makers. The data which follow regarding Australian sandarach are from the same source. According to Maiden it was a specimen of resin from the Oyster Bay pine of Tasmania, sent to the Exhibition of 1851, which first drew the attention of experts to the possibilities of Australian sandarach. For "the fine pale resin of the Oyster Bay pine (*Callitris Australis*) from the eastern coast of Van Diemen's Land, and other gums and resins, Mr. J. Milligan was awarded honourable mention" (Jury Report, 1851 Exhibition, p. 182). But for nearly half a century this product ran to waste.

Sources of Australian Sandarach. The Various Kinds of Cypress Pines.—The cypress pines all belong to the natural order coniferæ

(cone-bearers), and are therefore allied to the pines, firs, spruces, etc., of the Northern Hemisphere. They belong to the genus *Callitris*, which is mainly a synonym of *Frenela*. (The word callitris is from the Greek, *Kallos*, beautiful, in allusion to the appearance of the trees; Frenela is in honour of M. Frenel, a former member of the French Academy.)

In the Australian Colonies there are twelve species of *Callitris*, and some of them have varieties more or less marked, so that there are a goodly number of Australian cypress pines. Four of the species—*Rori*, *Drummondii*, *actinostrobus*, and *acuminata*—are confined to Western Australia, and have of course a limited interest in the Eastern Colonies. *C. oblonga* is only found in Tasmania.

There are no means of estimating the consumption of sandarach in this colony, yet New South Wales ought to be able to supply the local demand, and have a good surplus for export.

The cypress pines that are found in New South Wales are seven, namely:—

1. *Callitris macleayana*—"Port Macquarrie Pine," an elegant species now often seen in gardens. [No. 2 now included in No. 1.]

2. *C. parlatorei*—"Mountain Cypress Pine," "Stringybark Pine". These two species are closely allied, and are both found in the north coast districts. They are not as abundant, nor do they yield sandarach as freely, as the other species. [See No. 1.]

3. *C. verrucosa*—the "White or Common Pine," often simply known as pine or "Cypress Pine," but also as "Malee Pine," "Rock Pine," etc., and well known under its name of "Murray Pine". It is the most widely diffused of all the cypress pines, being found in every one of the mainland colonies. It is easily known by its rather ornamental warted cones. [Now divided into several species, chief of which is *C. glaucus*.]

4. *C. columellaris*—This is usually known as "Cypress Pine," and it attains a great size. It appears to be confined to the coast districts and moderate elevations of Northern New South Wales and Southern Queensland.

5. *C. Muelleri*—"Illawarra Pine," "Mountain Pine". This species is often very ornamental. Its range does not appear at present to be very well defined. Maiden has collected it at Middle Harbour, Port Jackson, and in the Blue Mountains (Mount Victoria). It has been sent to him from the Illawarra. Mr. Baker has collected it at Rylstone in the Mudgee district.

6. *C. cupressiformis*, perhaps better known by its synonym of *rhomboidea*. This pine Maiden has known to be a good deal confused in New South Wales with the preceding. Of course the cones are quite different. It is usually simply known as "Pine" or "Cypress Pine". It is extensively diffused in the coastal districts.

7. *C. calcarata*, better known under its synonym of *Frenela Endlicheri*. Everybody knows it under its name of "Red or Black Pine," whose timber is so largely used in the western parts of the

colony, where white ants are prevalent. There is no need to further allude to the species here.

Of the above, *C. verrucosa* and *C. calcarata* will be found by far the most important from a commercial point of view, but the others all produce excellent sandarach.

Chemical and Physical Properties of Australian Sandarachs.—Maiden's experiments tend to show this: Given similar circumstances in regard to size and age of tree, season of flow, climatic conditions, etc., the sandarachs from all the species are precisely similar in chemical and physical properties. Conversely it follows that if two specimens of sandarach are of different qualities, the explanation is to be found in the circumstances above enumerated. What is the best season to collect sandarach or to bleed trees in a particular district is only to be learnt by experience, and enough has been said to show that it is worth the trouble to try and find out. Australian sandarach burns readily, and on the Snowy River (near the Victorian border) it is often mixed with fat by the settlers to make candles. The aborigines used frequently to use it for a similar purpose. Sir Thomas Mitchell ("Three Expeditions," II, p. 37) says: "Each carried a burning torch of the resinous bark of the *Callitris*, with the blaze of which these natives (Lachlan) seemed to keep their dripping bodies warm."

1. *Callitris verrucosa*, R. Br. (syn. *Frenela robusta*, A. Cunn).—A sample of Murray pine resin from Quiedong, near Bombala, has a pale, bleached appearance, much lighter than ordinary sandarach. Externally it has a very mealy appearance. Water has no effect on it. In rectified spirit it almost wholly dissolves, leaving a little whitish resinoid substance. Petroleum spirit dissolves 5 per cent of a perfectly colourless and transparent resin.

Speaking of "Mountain Cypress Pine" or "Desert Pine" (*C. verrucosa*), the catalogue of Victorian exhibits, Colonial and Indian Exhibition, 1886, states: "A sandarach in larger tears than ordinary sandarach is yielded by this species. It yields it in considerable abundance, 8 or 10 oz. being frequently found at the foot of a single tree; but though this exudes naturally the supply is stimulated by incisions."

"It is a transparent, colourless, or pale yellow body, fragrant and friable, fusing at a moderate temperature and burning with a large smoky flame, very soluble in alcohol and the essential oils, and almost totally so in ether. Turpentine at the ordinary temperature does not act upon it, nor do the drying oils; but it may be made to combine with these solvents by previous fusion" ("Report on Indigenous Vegetable Substances, Victorian Exhibition, 1861").

This resin was used to make firm the union, after lashing, of the hardwood head to the reed in making of reed spears by the aborigines of Victoria. The resin was called by them Bij-jin-ne (Brough Smyth, "Aborigines of Victoria," I, p. 306).

A sample of New South Wales resin of this species is of a dark amber colour, and externally possesses the dull appearance found on lumps of amber. It is the darkest specimen of an Australian sandarach hitherto examined by Maiden. It almost wholly dissolves in rectified spirit, yielding a bright yellow liquid, leaving 2·5 per cent of an insoluble residue. Petroleum spirit removes 22·8 per cent of a clear resin when the original substance is digested in it.

Callitris verrucosa, R. Br. (syn. *C. preissii*, Miq. partly).—The following note by Dr. Julius Morel ("Phar. Journal," [3], VIII, p. 1025) in regard to a specimen of South Australian resin is interesting: "With sandarach resin may be connected another resinous substance which was exhibited in the Paris Exhibition of 1867 from South Australia under the name of 'Pine Gum'. It is the 'gum' of *Callitris preissii*, Miq. The product resembles sandarach, and might become an article of commerce. This resinous substance occurs in the form of slightly yellowish tears, thicker and longer than those of ordinary sandarach. In consequence of unequal contraction it presents, like sandarach, numerous facets, and consequently, the surface appears to be covered with a white powder. In its transparency and hardness the resin corresponds to sandarach. Its odour is very agreeable and balsamic, and the taste is bitter and balsamic."

2. *Callitris columellaris*, F.V.M. (syn. *Frenela robusta*, A. Cunn; var. *Microcarpa*, Benth).—A sample of resin from this species dissolves almost entirely in rectified spirit, forming a pale yellow solution. The insoluble residue amounts to 4·6 per cent. Petroleum spirit when digested on the resin removes no less than 35·8 per cent of a transparent colourless resin. This is a remarkable percentage, and it would be interesting to inquire whether Australian sandarach becomes increasingly soluble in that menstruum by age. An ordinary sample of commercial sandarach yielded 8·9 per cent to petroleum spirit.

3. *Callitris cupressiformis*, Vent (the "Oyster Bay Pine of Tasmania," partly).—This is the pine already referred to, and a brief account of the resin has been copied into many of the textbooks. Maiden has collected resin of this species from Port Jackson clear and transparent as water. It turns pale amber colour if placed in a bottle, but its brilliancy shows no sign of diminution in that time. The Sydney trees readily exude their resin on slightly wounding, and the same remarks apply to the Tasmanian.

4. *Callitris calcarata*, R. Br. (syn. *Frenela Endlicheri*, Parlat).—A sample of red pine resin from the Lachlan River has freshly exuded, and has the colour and appearance of the best selected sandarach. Rectified spirit nearly wholly dissolves it, forming a beautifully clear, slightly yellowish fluid with 1·3 per cent of residue. Petroleum spirit extracts 22·1 per cent of an apparently perfectly colourless and transparent resin.

Tested against Mogadore Sandarach.—The *Callitris* resins soften

slightly but do not melt in boiling water, and a sample of commercial sandarach behaved similarly. In the mouth they feel gritty to the teeth and in no way different to Mogadore sandarach. When freshly exuded they are very irritating to a cut.

The properties of Mogadore sandarach are shared by Australian sandarach. Maiden does not know in what respect they differ, and the one article may, he says, be substituted for the other.

Australian sandarach as it comes to the London market consists of much larger but non-transparent tears. Moreover, the yellow cast is not nearly so decisive as in Mogadore sandarach. According to Mr. Clark (R. Ingham Clark & Company), the Australian resin is very similar to Mogadore, and a very average sample of the former might, if properly washed with a weak solution of potash, equal the finest picked Mogadore sandarach selling at the date of Mr. Clark's report, October, 1894, at 70s. per cwt.

For the purpose of having a recent and reliable opinion in regard to these sandarach resins samples were sent by Mr. Maiden to the Director of the Royal Gardens, Kew, who kindly obtained the opinion of Mr. Robert Ingham Clark, a well-known authority in regard to such substances.

Mr. Clark reported: "For the purpose of comparison I have sent you some samples of the Mogadore sandarach, with their present market prices attached, which will approximately give you the values of the New South Wales kinds.

"In character they are very similar, and could be used for the same purpose, excepting that the sample marked No. 2 after solution in spirit is inclined to crystallize out, which would be fatal to its use in spirit varnish. Mogadore samples are in a much cleaner and finer graded condition; and it would be advisable to suggest that these latter kinds should undergo some system of washing, sifting, and sorting before being placed on the London market, there being a very material increase in value for what to the eye appears a small improvement only. Samples sent with their to-day's (31 October, 1894) value.

"1342. Fine picked sandarach, 70s. per cwt. If your sample No. 1 was thoroughly washed and sifted it might equal this.

"1345. Fine sandarach, 60s. per cwt.

"1347. Ordinary sandarach, dusty, 47s. per cwt.

"I think if your sample were washed in a weak solution of potash it would remove the outside coating."

In concluding these remarks on Australian sandarach, it can only be urged once more (as in this treatise, Edn. I), that Australian sandarach has not hitherto received from British spirit varnish manufacturers the attention to which its intrinsic merits entitle it, and which have only to be known to be appreciated.

Australian Sandarach from Victoria.—Cordemoy gives the following particulars as to an Australian sandarach resin from Victoria. Australian sandarach (he says) is furnished in great part by the

Callitris verrucosa, R. Br. (*Frenela verrucosa*, A. Cunn). This conifer, the botanical characters of which greatly resemble the African species, inhabits the desert regions of the north and north-west of the Colony of Victoria. The resin exudes spontaneously from the trunk often to the foot of the tree, but the quantities obtained are more considerable if the exudation be stimulated by methodical incisions. This product is met with in large stalactitic masses consisting of numerous elongated tears or in fragments of various sizes. All the pieces are covered with a whitish dust due to superficial oxidation, but the fracture is brilliant and shows in the interior a pale yellow, limpid resin, of a pleasant smell but rather faint. This substance is friable and is easily pulverized. It is completely soluble in alcohol and in ether. When cold, spirits of turpentine has no action on it. If a mixture of this resin and spirits of turpentine be heated on the water-bath, it does not dissolve, but gradually softens, and is transformed into a pasty, stringy mass which adheres to the bottom of the dish. But the resin melts very easily at a moderate heat. If boiling turps be added to the fused substance, solution takes place without difficulty. A sample of resin of unknown origin from Queensland was found to resemble Australian sandarach in its properties. The latter is obtained in the form of small yellow tears from *Callitris calcarata* and *Callitris verrucosa*. The following figures show the resemblance between the two resins :—

	Specific Gravity	Acid Number.	Solubility.
Queensland resin .	1·0543	136·6	Sol. in alcohol or ether.
Australian sandarach	1·060	135·8	„ „ „

African sandarach, obtained from *Callitris quadrivalvis*, brings the highest price in the market, but this is probably due to its regularity, as there is no essential difference between this and the Australian variety.

[Since the above was printed the botanists and chemists of the technological museum, Sydney, Messrs. Baker and Smith, have published a monograph on the Australian pines, the predominant genus of which is *Callitris*, but beyond separating the *Callitris* from the *Thuya* and the creation of the latter into a distinct species by itself, and the splitting up of some of the species described above into two or more distinct species, there is no real information of any practical value as regards sandarach, except the testimony of numerous heads of schools that it flows abundantly, especially when wounded. Araucaria resin and Kauri resin are, however, well described, and one rises from a perusal of the book and its illustrations with the firm conviction that all three species of pine trees, Callitris, Araucaria and Kauri, could be successfully tapped on the cup and gutter system both for turpentine and resin, and that this would have been done ere now if Australia had been a French colony and not a British one, in proof whereof France many years ago introduced the cup and gutter system into New Caledonia.]

CHAPTER XIX.

SHELLAC.

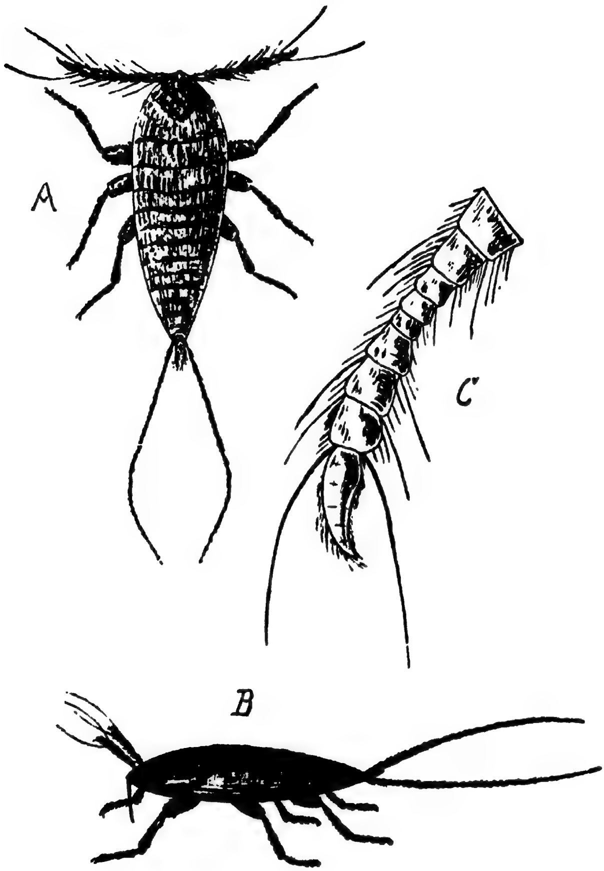
Shellac.—Shellac, the raw material *par excellence* of the spirit varnish-maker, is a secretion of the *Tacchardia lacca*, an insect allied to cochineal. Shellac, according to Tschirsch, consists of wax, colouring principle, and pure resin, and has the following percentage composition:—

TABLE LXXX.—COMPOSITION OF SEED LAC (FARNER).

	Per cent.	
Wax	6·0	Myricil and ceryl alcohol, free and combined, and melessic, cerolinic, oleic, and palmitic acids.
Colouring principle .	6·5	Identical with Schmidt's laccic acid.
Pure resin . . .	74·5	Soluble in ether 65 per cent. Insoluble " 35 " "
Residue . . .	9·5	Sand, woody debris, insect remains, etc.
Water loss, etc. . .	3·5	
	100·0	

The *Tacchardia lacca* lives on the juices of the tree on which it feeds. It sucks these juices up by a proboscis. The adult female cannot move, but the mature males emerge from their pupal cases, and, assuming a pair of long transparent wings, fly off to visit the females and soon after die. The larvæ swarm at two different seasons, sometimes three, July and December, or also January. The larvæ emerge from the dead bodies of the females and crawl off in search of fresh feeding grounds. At this stage they are minute orange-red creatures with no perceptible separation into head, thorax, and abdomen, but with fully-formed feelers and powerful legs. But nothing differentiates them into male and female; they measure about $\frac{1}{40}$ of an inch. The swarming lasts some days, until the twigs are quite red and actually alive. Most, however, perish; only a fortunate few are entrained, by the wind, or by bees, birds, or squirrels, or by their own unaided exertions, to fresh spots, where they fix themselves, and the now useless legs disappear. A resinous excretion, which is essentially different from a secretion, soon begins to accumulate around the bodies of the insects, and this excretion, to which each insect contributes its contingent, swells to such an amount as to encrust the twig com-

pletely. If a longitudinal section of the encrustation be now made, the section shows a cellular structure with two descriptions of cells,



A Young male larva, after swarming, dorsal view, x about 250

B do do side view, x about 250

C Antenna of above, further enlarged

FIG. 87.—*Tacchardia lacca.* The lac-secreting insect (after Suter).

large, circular caverns, more numerous (females), and smaller, oval cells (males). About two and a half months after swarming the males escaping from their cells assume wings (*vide supra*) and flutter

away to visit the females. Soon the bodies of the females enlarge, and assume a bright red colour. She develops viviparous larvæ and dies, her body becoming the incubation chamber of her numerous progeny, about 1000. These escape by swarming, and so this cycle of insect life and death re-occurs twice annually.

If we examine a piece of stick lac, that is, the resinous matter on a twig, by the microscope, we find it pierced by numerous small, rounded orifices. Two small whitish spots are to be seen near the rim of these orifices. A section of the same lac, previously detached from the twig, consists of three layers; a medium layer full of alveolar cavities, separated from one another by thin partitions of resin, and two other layers (cortical) lying on both sides of the preceding, the internal one very thin, the external one much thicker, both compact but traversed by whitish trains leading to medium-sized cavities on the periphery, where their extremities form the above white spots. The female insects settle on the young twigs.

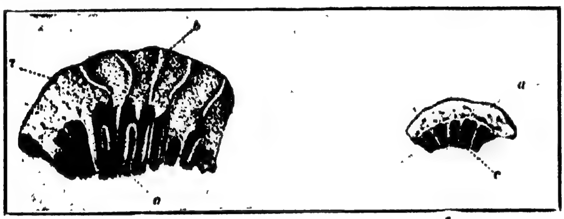


FIG. 88.—Spherical segments of Madagascar Shellac. 1, After nature, natural size (Cordemoy): *a*, external resinous layer; *c*, cells occupied by the insects; 2, after Targioni Tozzetti, segment enlarged three times: *a*, external resinous mass; *b*, whitish waxy trains; *c*, broken extremities of the insects dwelling in the cells.

They are solitary or often grouped side by side. They fix themselves by their anal extremity, furnished with long, silky, maxillo mandibularies. They surround themselves with a reddish-violet layer of resin. But from the periphery of this layer the anal tube emerges, possibly retractile, which they carry at their posterior. Each rounded orifice observed on the surface of the crude lac corresponds, therefore, to the anus, and it was from these orifices that Carter saw the young emerge. Moreover, on each side and at the base of the anal tube of the insect, two large mamillary tubercules are found, which Comstock regards as the lac-secretion organs. These tubercules, situated near the posterior stigmata, exhibit at their base webs which yield a porous wax. Again, the less important waxy deposits of the internal layer are produced by webs placed near the anterior stigmata. This wax forms those whitish trains which traverse the compact cortical layers of the lac and come out at the surface. These trains of permeable wax place the tracheal apparatus of the insect in contact with the air on the outside. They are in direct relationship with the respiratory func-

tion, because when the cochineal is entirely submerged in the resinous mass they ensure free access of air to the stigmata. The alveoles of the middle plurilocular layer in which the insects dwelt are empty, or lined on their surface by a pulverulent coating of white wax, or again filled with the red colouring matter, also pulverulent, which, according to Carter, is contained during life in the ovary of the insect. From this fact he deduced this practical rule, that to obtain lac with a maximum of colouring matter the shellac should be collected, at least in India, in the end of May or beginning of June, i.e. before the birth of the larvæ, which carry with them the greatest part of this colouring matter. The wax in the lac is not therefore mixed with the resin; it forms distinct deposits and plays a special rôle in the biological history of the insect. When a piece of stick lac is suspended for some time in 95 per cent alcohol the resin dissolves and the wax appears as whitish threads, forming pencils, hung to the cells formerly occupied by the insects. If, therefore, there can be no doubt as to the origin of the wax, that of the resin is less certain. However, the opinion of Carter, and of many other observers, that the resin is not an exudation of the tree but a secretion of the insect itself, is generally accepted. If the vegetable origin of the lac were accepted, it would be difficult to explain how lac possessed the same properties upon whatever plant it be produced, the more so as the greater number of lacciferous trees do not exude resin of any kind.

The following summary is quoted from Watt:—

"(1) There are two broods, the swarming of larvæ taking place in July and again early in December. (2) It is commonly stated that the proper seasons to collect lac are in May and June for the one and October to November for the other crop, but it is believed that these periods were fixed with a view to preserve the dye as well as the lac. (3) Up to the emergence of the larvæ the female insect is alive, and is continuing the process of formation of the lac. If the dye be of no consideration whatever, collection might be delayed until the escape of the larvæ, and the consequent death of the female. 'Stick lac gathered after the insect has emerged is known in Lohar-Sugga district by the name of Phunki. It yields scarcely any dye, but is very good for working into shellac ("Statistical Reports," Vol. II, p. 406).' (4) The seed twigs intended for propagation should not be removed until immediately before the period of swarming. Should seed twigs be cut off before maturing is attained the loss of supply of sap in the twig would kill the mother insects, and the brood be lost in consequence. The failures that have attended the attempts to send seed twigs from one part of India to another have been due mainly to the fact that the seed twigs were cut too long before the swarming period or too near it. In the latter case the larvæ would escape during transmission, and finding no fresh twigs upon which to become attached would of necessity perish. (5) The larvæ are so minute that the seed twigs must be carefully

attached to plants upon which propagation is contemplated. A string tied across the twig will often suffice to check the swarming, and the larvæ may be seen in thousands in the vain effort to pass underneath the string. The best way is to impinge the seed twigs across the bifurcations of the smaller branches of the tree. (6) The larvæ are so minute that they are doubtless carried from tree to tree by wind, by birds, and by insects. It has been sometimes contended that the lac insects do not injure the trees. Apart from the improbability of this assertion, nature seems to provide for a migration, and it appears, therefore, possible that the deterioration in quality often complained of may be due to too long cultivation on the same trees; but in this connexion I may add that the Collector of Monghyr recently sent me a few twigs of the peepal tree with lac encrustations on them, accompanied by a statement that the older peepal trees of the district were all being killed by the lac. But these trees possibly sheltered a different species of the insect. A very full account of the natural history of the lac insect will be found in a paper by H. J. Carter, F.R.S., in the 'Journal of the Agricultural and Horticultural Society of India' (Vol. XI, Pt. II, 1859-60)."

Watt summarized the reproduction of lac as follows:—

"The system of propagation that at present prevails consists in lopping off a few twigs a little before the expected date of swarming. These are carried to fresh trees, or fresh boughs of the same tree, and tied on convenient and suitable positions. The larvæ on swarming crawl to new (? young) wood and become fixed. If the object in the collection of lac be to procure the red dye, the stick lac, that is, the lac-encrusted twigs, should be gathered before the larvæ have swarmed. But if the resin lac be sought there would seem to be reason to delay collection until the swarming has taken place. The industry assumed its present form while lac dye, if not equally valuable with the resin, was a profitable by-product. It is now valueless. Its presence admittedly depreciates the shellac very greatly. It necessitates expensive, and possibly to the resin injurious, methods of removal, and the decomposition of the larvæ gives the offensive smell to the factory which wellnigh becomes a public nuisance. It would therefore seem that the time has more than come when this state of affairs might be mitigated by some change in the season of collection that would allow of the colour being very largely removed before the stick lac comes to the factory. The collecting seasons at present adopted are May to June for the one brood and October to November for the other. A delay of a month or six weeks in each case would see the swarming accomplished." But that the lac dye is an unmitigated evil seems a pessimistic view; however, the point is would this delay improve elasticity, etc., as well as colour? In any case, why not improve the methods of extracting lac dye so as to put an article of such excellence on the market that if it cannot command its own price would at least be

assured of a recognized position. That this point has not been seen to before now is due to the inertia and *laissez-faire* attitude of the typical East Indian official. A really practical chemist should have no difficulty in utilizing shellac dye at a profit, and that too without injuring the shellac. This insect builds up this valuable dye at the sacrifice of its life for the spirit varnish-maker and shellac-bleacher to destroy it by chlorine. We seem still to live in a rude and barbarous age when that is the best we can do with our twentieth-century technical education.

Watt discusses the question as to whether the well-known different qualities of lac are due to the plants on which it feeds, but believes that the grades of lac are due to being the resins of different species of insect. He urges that the lac insects found on leguminous plants or soft-wood plants, such as *Butea frondosa* and *Cajanus indicus*, can with difficulty be induced to live upon hard-wooded trees like *Schleichera trijuga* and *Shorea robusta*, on which lac is nevertheless found. He further urges that there are special cultivated races, e.g. those on *Acacia Arabica*. In Sind and adjacent tracts that plant is used as food stock, but hardly anywhere else is lac to be seen on that tree. Watt urges still further that here we have a special race or a remarkable climatic adaptation. Further, Watt states that all over India albino broods have been recorded as occasionally seen. Watt concludes that were the selection of stock placed on a rational and scientific basis, improvements in quality might be effected if it were not possible actually to evolve a white insect, or at all events one to a large extent devoid of the objectionable colour, the removal of which so seriously enhances the cost of the present-day resin (Watt). But Watt's opinion is more that of the naturalist than that of the physiological chemist. On a tree which secretes a red tanno gum (kino) like the *Butea frondosa* even an albino insect might eventually secrete coloured lac. Surely a tree with a coloured juice is more likely to produce a coloured lac than a tree with a colourless juice. Watt goes on to say that the insect lives upon a large number of widely different plants. In the "Agriculture Ledger" he has given the names of fifty-six trees. Those best known are *Butea frondosa*, *Ficus religiosa*, *Schleichera trijuga*, *Shorea robusta*, and *Zizyphus jujuba*. These he says are all trees indigenous to India, so that the lac got from them may be called wild lac; but two plants are specially grown for it, and here the lac insect is a plantation product and exists under a greater degree of cultivation than the wild insect. The plants specially grown are *Acacia Arabica* in Sind, and *Cajanus indicus*. The culture of the *Cajanus indicus* is also pursued for this purpose in French Indo-China. But Watt confesses that lac cultivation does not, at least in many localities, pay as a special plantation product. The crop, he states, is most capricious, both in yield and price—one year highly profitable, the next the margin so narrow that there is no inducement for extension. In witness whereof Watt quotes :—

Exports—Shellac.	Cwt.	Value.	
1902-3	195,000	1,048,991	That is to say, in 1903-4 17,290 cwt. less was exported, but the total value was nearly half a million more than in 1902-3.
1903-4	178,000	1,456,067	

The fluctuation might have been the other way about, viz. a loss. It is not surprising that with such fluctuations the supply should also fluctuate.

Hail and rain often kill and wash away thousands of colonies of insects. Birds and monkeys damage them considerably, as do ants, who swarm up the trees to feed, as some say, on the sweet secretions of the insect. But Giard does not see that the ants are enemies of the cochineal, their relations with which have been badly understood. Their relations are mutualistic and in no way predatory or parentic. But in any case it is not advisable to try to produce lac where these insects prevail. A black fungus forms over the excrescence of the insect, and is often mistaken for a pest, but is in fact quite harmless. The caterpillar of a small grey moth attacks the insects and devours them greedily. It appears that this occurs only with the winter crop.

Cost of Production.—The following estimate is based on the actual experience of an Assam planter:—

TABLE LXXXI.—AN ASSAM PLANTER'S SHELLAC PRODUCTION PROFIT AND LOSS ACCOUNT.

	Rs.
Rent at Rs.3 per acre for 80 acres	240
Hoeing or cutting jungle between trees	320
Upkeep of necessary buildings	100
Cutting branches and putting in seed	340
	1000
Manufacturing charges at 5 per cent	3500
Packing and dispatching at 2½ per cent	1750
Calcutta charges for forwarding and river freight at 2½ per cent	1750
London charges for sea freight, dock and brokers' charges	3000
	11,000
Proceeds of sales, 1750 at 14d.	26,250
Deduct discount to buyers	656
	25,594
Deduct expenditure	11,000
	14,594

In the case of lac worked in connexion with tea or coffee, the amounts for European and native supervision and upkeep of coolie lines, etc., may be added proportionately according to circumstances. The planter referred to, however, lost nearly his whole crop next year from the attacks of a night moth.

Stick Lac.—The lac-encrusted twigs collected from the trees

(first crop May to June, second crop October to November) are known as stick lac. The encrusted twigs are cut into short sticks (2 to 3 inches long) and dried in the shade. In drying the wood shrinks so as to leave the stick lac as hollow tubes, but still with much adherent wood, bark, debris, etc. The cutting up of the twigs into pieces of a uniform short size facilitates packing in bags, in which it is conveyed to market and sold through different brokers to the manufacturers. In fact, the stick lac passes through the hands of many middlemen before it reaches the factory. Take Assam lac: the actual cultivator sells the lac to a Garo trader at the foot of the hills; he, in his turn, sells it to a Bengali trader at the markets of Jira, Nibari, and Damra; it is then carted to Goalpara, and purchased by a Goalpara merchant, who ships it to his agent in Calcutta, who now disposes of it to the Calcutta manufacturers.

Watt quotes a quaint practice usually followed in most sales of lac. The buyers and sellers join hands and sit facing each other, a cloth being thrown over the hands. The buyer presses certain fingers of the seller's hands, thus making an offer. This is usually rejected by making a motion of the head, and further finger-pressing ensues. Finally the bargain is struck without uttering a word.

Stick lac is only imported into Great Britain in much smaller quantities than the prepared lac. Users shirk the trouble of separating the lac from its matrix of bark and woody fibre. Not even the assurance that here, at least, they are handling the genuine article will induce them to do so. The reason is not far to seek. The spirit varnish industry was for a long time a hole-and-corner business, carried on by small men who, making a big profit on their small output, were too purse-proud and too little inclined to get out of the rut in which they moved. The labour incidental to their operations was almost *nil*, and they took good care it stopped at that. The less mankind has to do the less he feels inclined for further exertion. But in these days of technical education British varnish-makers will, it is to be hoped, see the force of importing the stick lac direct, and of working it up for its dye for use as a varnish stain. What a ridiculous caricature of twentieth-century technical education it is to remove the dye inherent to shellac only to replace it by Bismarck brown. Besides forming *per se* an excellent natural spirit varnish stain, lac dye could be utilized in the coloration of oil varnishes and to make coloured rosinates and resinates for spirit varnish-making.

Seed Lac.—This consists of the stick lac ground and crushed to rounder pieces, corresponding so far to the female cells. The dust is termed *Khud.*

Preparation of Lac Dye and Lac Lake.—The pure sifted seed lac is washed in large stone troughs and left covered over with water for twenty-four hours. The wood which floats to the top is removed, dried, and used as fuel. A man or woman now enters the trough or tub, and seizing hold of a cross-piece at a suitable height,

treads with the bare feet on the granular lac and presses it against the sides and bottom of the trough, after the style of the Scottish peasantry in blanket washing. The lac is thus broken up into a still more finely granular condition, and the water becomes of a deep claret colour. This deep-coloured water is run away, and the washing repeated till the wash water comes away colourless. The washings can be evaporated down and pressed into cakes so as to form lac dye. The washed granular resin is now called *washed seed* lac, and is sifted into two grades, granular and dust (*gaud*). When machinery driven by steam is used in the lac factory, after the stick lac is passed through the mill and sifting, the ground lac returning to the crusher everything that does not pass through the sieve, the sifted product is stirred with beaters in a revolving cylinder with a weak solution of caustic soda which dissolves the colouring matter; the alkaline solution is decanted, and a solution of alum added which precipitates this colouring matter and the fraction of shellac dissolved by the alkaline lye.

FIG. 39.—Stick Lac produced on a branch of *Cajanus Indicus* spruce, (after Cordemoy).

The precipitate is pressed into cakes which are dried in the sun. A product is thus obtained which contains 50 per cent of colouring matter.

The colouring matter of lac was prepared in India and was extensively used as a scarlet dye-stuff, for the production of which it was a most efficient substitute for cochineal. Two forms of it were imported, called lac lake and lac dye. These substances contain about 50 per cent of the colouring matter, mixed with more or less of the resin, and with earthy matters, said to consist chiefly of chalk, gypsum, and sand. According to Dr. Ure ("Dictionary of Arts," etc.), the cakes of lac dye imported from India, stamped with peculiar marks to designate their different manufactures, were employed exclusively, in England, for dyeing scarlet cloth, and were found to yield an equally brilliant colour, and one less easily affected by perspiration than that produced by cochineal. The solvent of the lac dye is dilute sulphuric or hydrochloric acid, especially the latter, and the proper mordant is stannic chloride and tartar.

The details of the process were given by Ure and by Dumas. The general characters of the colouring matter of lac appear closely to resemble those of cochineal and kermes.

The demand for cochineal, says Watt, served the useful purpose of pointedly directing attention to the lac dye. This, though inferior, was quite good enough for most of the purposes to which cochineal was put, and had the advantage of being considerably cheaper. A large trade in lac dye accordingly sprang into existence that gave the impetus for numerous lac factories owned directly or indirectly by the East India Company. At this time was invented, and by Europeans doubtless, the method of manufacturing lac dye

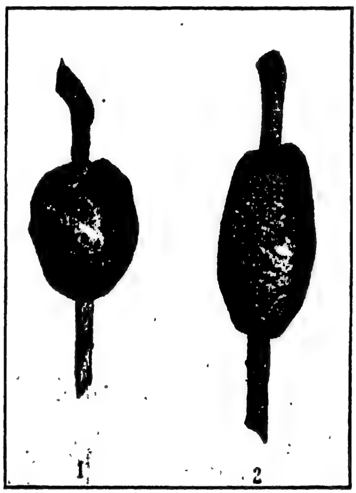


FIG. 40.—Madagascar Lac in two most common forms: 1, globular form; 2, ellipsoidal form.

into special cakes ready for use. Such importance did this assume that it dwarfed the gum lac of the earlier commerce until it might almost be said that the resin (lac) became a by-product of the lac dye factory. To this circumstance is due the fact that the methods of cultivation, of collection, and of manufacture, were invented and perfected with a view to produce the dye, one might almost say at the expense of the resin. The dye gave the profit to the industry, but Sir W. Perkin's discovery of aniline struck at once the deathblow of both the Mexican cochineal and the Indian lac dye industries. By this time, however, new methods and directions of using the resin lac had been discovered in Europe, and the interest of the factory shifted until the dye became first the by-product and ultimately the useless waste or material of the factory. Here, then,

we are presented with a demonstration of the startling fact that a by-product, that can be produced at an almost nominal cost, cannot of necessity contest the market against the products of the chemical laboratory. Attention was thus concentrated on the resin, and it soon became the chief features of interest. James Kerr ("Phil. Trans.," 1781, Vol. LXXI, p. 374) was one of the first to mention and describe the manufacture of shellac. From about that date, therefore, the modern factory industry may be assumed to have originated.

In some places the seed lac after treading in the tubs is washed or even boiled in crude carbonate of soda lye, or in one of soda and borax, or of crude carbonate of potash, or in borax alone, or of aliens, after which it is almost white. But in the larger shellac factories seed lac is not washed in any of these lyes, but repeatedly washed in pure water, but not bleached. Some allege that bleaching weakens the lac. After washing, or washing and bleaching, the seed lac is spread over special floors exposed to light and air, by which it is thoroughly dried and still further bleached.

The dried washed seed lac is now mixed with certain ingredients according to the object in view. One of these is orpiment-arsenious sulphide (yellow arsenic) As_2S_3. This substance is often unwarrantably classed as an adulterant. But Watt gives good reasons for its use. According to Watt, "the arsenic is said to make the lac opaque and a rich straw colour, but its action would appear to be mainly, if not entirely, mechanical". But that, in our opinion, only half states the case. Before the arsenious sulphide can act mechanically it must first combine with one or other of the ingredients of the shellac in the same way as the red sulphide of antimony does with rubber. The rôle which orpiment plays in shellac manufacture is therefore a vulcanizing one, and to the orpiment in great measure is due the nerve and spring and elasticity of orange shellac. Watt freely admits "that the hand-made machinery lac possesses certain properties never attained by the steam machinery factories". This is due very evidently to either the non-absorption of the yellow arsenic or to its bad admixture at an unsuitable temperature with the shellac. This point can be settled definitely by determining the breaking strain of the various grades of pure shellac made by fire-heat and steam-heat respectively, establishing the relation between thickness and breaking strain, and doing the same with orpiment-treated shellac made by fire-heat and steam respectively. But to condemn orpiment as an adulterant, as was done recently, because orpiment was found untouched in the French polish vats, is radically unsound. It may be liberated in these vats in the free state by a thousand and one different causes. If vulcanized rubber were dissolved in terpineol, which is said to act as a solvent, antimony sulphide if it were the vulcanizing agent used would undoubtedly be found as a residue from a rubber so treated. Therefore, to follow the logical conclusions of

these observers, antimony sulphide, in all conditions, is a rubber adulterant. Attempts have frequently been made to replace arsenious sulphide, but Watt says: "The inquiry for a substitute for arsenic has often been made though not as yet supplied. *A yellow colouring material that will fuse into the lac when subjected to the temperature of* 35 *lb. steam power is required*". Mark the word "fuse," that can only mean that the orpiment dissolves in the shellac. Mark again that a substitute is not required for orpiment at a fire-heat. Why? Possibly because orpiment does its work very well with fire-heat but not so well with the lower steam. These criticisms are put forward, not as ascertained facts but as points to be investigated before deliberately denouncing orpiment as an adulterant. Possibly zinc sulphide might replace orpiment.

Coming to rosin. Here again, "the object of the rosin," says Watt, "is to lower the melting-point, a condition essential to many industries and one known from fairly ancient times (witness Acosta's allusion to it in 1578). *Its value, therefore, is fully recognized, and a certain amount is not only admissible by the rules of the trade* (2 to 3 *per cent*), but few of the shellacs that are regularly exported can be said to be entirely free from rosin. During seasons of high prices the proportion is often, however, raised until it passes from the condition of permissible admixture to what might be called criminal adulteration." But to call a substance when used in a judicious, and in the eye of the trade a perfectly legitimate, manner to lower the melting-point of shellac so that it will so far melt without such charring or decomposition, that it does not lose after fusion all the good properties that it had prior thereto, an adulterant, is to fail to see matters in their proper light and in their true proportion.

Melting Lac—Hand Process.—The arsenious sulphide or orpiment As_2S_3 is ground to a fine powder and then mixed with the pulverized rosin and with the specially bleached and washed lac, and then the thoroughly uniform mixture is run into long narrow bags 20 feet by 2 inches. For one quality of lac American drill is necessary, for another a cloth specially made at the Cawnpore cotton mills is used. After being charged the bag is arranged in front of a long open fire and so arranged that the attendants can twist it as it is being slowly moved along. The man in charge sits on a little raised mud platform immediately to the left of the fire and somewhat behind it. He holds the end of the bag in his left hand and apparently at the outset does not twist the bag but simply resists the twisting action produced by his assistant. The fused lac in the portion most exposed to the dry heat is thus squeezed through the bag. Every now and then the leading hand gives his end of the bag a twist in the opposite direction to the twist of his assistant, and thus the portion from which the lac has been removed coils up like a rope. The bag is drawn forward very steadily as each portion in its turn is exhausted. The foreman wields at intervals three weapons: (1) a long iron-hooded poker with which he stirs the fire;

(2) a wooden spoon with which he every now and then sprinkles with water the tiled floor in front of the fire; (3) an iron scraper with which he removes the fused lac as it oozes on to the surface of the bag and allows it to drop on the damp floor. If not sufficiently cooked the fused lac is picked up from the floor and once more placed on the top of the bag and re-fused (two to three times). Great skill is required in knowing when the lac is cooked to the proper extent. Hand-made lac possesses certain properties never attained by steam machinery factories. Eventually the whole of the contents of the bag are wrung through it; they drip as just seen on the floor in front of the fire or into troughs containing water or on heated stone flags.

Shellac.—The next stage in the process is the conversion of the lac into sheets. A sufficiency of lac in a state of fusion is passed to an assistant, who places it in an earthen or zinc tube filled with hot water fixed in the ground at an angle of 45° to the floor (or on a green banana stem). The molten lac is spread out by aid of a ribbon of palm-leaf and stretched between the hands into a thin skin, say an eighth of an inch thick. But though this looks easy it requires great skill to be able to use the exact dexterity to induce the lac to distribute itself in a compact uniform sheet. This sheet or skin is clipped off the tube and then handed to still another assistant, who bringing it in front of the fire grasps it between his toes, teeth, and hands, and widening his legs as he expands his arms and straightens both body and neck, draws or stretches the sheet out into one of three or four times the size of the original, and thus reduces it to the thinness of tissue paper. It is then laid on a mat and allowed to cool gradually (Watt). When quite cold the sheets are assorted according to colour, after all impurities and darker portions have been removed. When the select pieces are broken up they constitute what we know as shellac. But no part of the lac is rejected altogether. The pieces rejected either go to make up lower grades or are again mixed with dark-coloured seed lac and used up in the making of grades in which colour is of no object. The refuse retained by the melting bags is removed and the bags are boiled with a little alkali, and the resulting extracted lac is made into cakes 6 inches in diameter and 1 inch or more thick and is known as *kiree*. These, according to Watt, are possibly the "great cakes" alluded to by the East India Company as procured in 1816 from Agra, as also the lump lac of their early commercial returns. These cakes are sold, like the "khud" and "gaud," to the manufacturers of sealing-wax, bangles, toys, etc., and by the cabinetmakers such crude lacs are largely employed to cover up cracks in wood. Exported it is used for cheap French polish. Only in the case of TN and a few other brands is it specially stipulated in contract notes that the bulk on delivery must not contain more than a certain percentage of rosin. Many grades of shellac are simply bought on the stipulation that the bulk is to be equal in quality and colour (not in condition) to a

sealed sample in the broker's office. When the delivery comes to hand a sample representing 10 per cent of the bulk is taken and adjudicated on by the buyer and the broker. If they disagree the dispute is referred to two arbiters, who decide generally on the comparative physical properties of the sample. They may call also for an analysis. If the arbiters disagree an umpire settles the dispute, and he also can call in the aid of a chemist if need be.

Shellac comes to the London market in either a "free," "matted," or blocky condition. The shellac is described as "free" if its constituent leaves are not cemented or agglomerated in any way. It is described as "matted" when the leaves are agglutinated together by the high temperature it undergoes on the voyage, say in passing through the Red Sea. The shellac is described as "blocky" when the constituent leaves have become consolidated or caked into blocks which require mechanical effort to separate them. The state in which shellac comes to the port of delivery is a matter of vital importance, as it may be in such a condition as to be unsaleable except at a sacrifice. If the ownership of shellac bought c.i.f. passes to the buyer the moment the consignment is put aboard at the port of export, and all that happens to it in transit, is at the owner's risk, yet shellac sold for forward delivery must be delivered in good marketable condition. D.C. (David Campbell) is the best brand.

Button Lac is only another form of shellac, made by allowing the melted shellac to drop into rounded pieces, about 1 inch in diameter. It is only different from shellac in form. Instead of being made into thin sheets the melted shellac is poured on to plates in such a manner that it sets in the form of a large round flat piece, which, owing to its thickness, appears of a dark brown colour, but is of a dark ruby colour on being looked through. Button lac occurs, as does "tongue lac," in roundish or elongated cakes, and varies from pure to a mixture of upwards of 50 per cent of rosin. Dealings in this are usually by sample. In button lacs, the finer qualities often have the manufacturer's mark stamped on each individual button, the pure grades especially, and here again we have a great variety of these marks. It is usually sold in various standards, each of which is allowed to contain a specified amount of rosin. Button lac, therefore, is differentiated from others more by the slight differences in manipulation which are necessary when the button form has to be made and by the form in which it comes to market. In its preparation the molten material is not stretched at all but is simply allowed to drop on to a smooth substance such as a green leaf taken from the banana stem, and here it may be as well to repeat that garnet and button lacs contain, as a rule, no arsenic, though they may possess a high percentage of rosin.

Garnet Lac, in thick more or less flat pieces, is always understood to be a mixture of 90 per cent lac and 10 per cent rosin, and if it does not come up to this standard in London allowances have to be made. It is very similar to button lac, but is made into thick flat

pieces which in colour resemble those of button lac. Usually the quality of lac made into button or garnet lac is not so good as that from which orange shellac is made.

In the production of garnet lac the sheets are taken at the hot tube stage, no further stretching being necessary. Garnet lac is, however, very largely the product of the steam power factories. As its name implies it is of a deep, rich red colour, and is in demand for industries where colour is not a disadvantage (Watt). For the manufacture of certain garnet lacs solution in spirit, filtration, and recovery of the solvent are said to be practised. Of garnet lacs few brands are known, the reason being that as it is mainly a steam-power factory product it seems to be made by only a limited number of makers. The best quality is AC (Angelo, Calcutta); then GAL, probably a Hindustani word; LALL (red), and KALA (black), both Hindustani words. Garnet and button lacs contain as a rule no arsenic, though they may possess a high percentage of rosin.

It was, for a long time, a great desideratum among artists to be able to decolorize shellac, as if its dark brown hue were eliminated, it would then possess all the properties essential to a good spirit varnish in a higher degree than any other known resin. A premium of a gold medal, or thirty guineas, for "a varnish made from shell or seed lac, equally hard and as fit for use in the arts as that prepared from other substances," was offered for some years by the Society of Arts. The editor of the "Franklin Journal of Philadelphia" observed, in reference to the foregoing, that "these ends are perfectly attained by the process given by Dr. Hare, which leaves nothing to desire, excepting on the score of economy". "Dissolve (says Dr. Hare) in an iron kettle 1 part of pearl-ash in about 8 parts of water, add 1 part of seed or shellac, and heat the whole to ebullition. When the lac is dissolved cool the solution and impregnate it with chlorine until the lac is all precipitated. The precipitate is white, but its colour is deepened by washing and consolidation; dissolved in alcohol, lac, bleached by the process above mentioned, yields a varnish which is as free from colour as any copal varnish." About the same period of time as the publication of the foregoing, the before-mentioned premium of the Society of Arts was claimed by two persons, Mr. George Field and Mr. Henry Luning. The Society, upon due examination of the processes and products, found them both to answer the intended purpose, and awarded the sum of twenty guineas to each of the candidates. The following is Mr. Field's process: Six oz. of shellac, coarsely powdered, are to be dissolved by gentle heat in a pint of spirits of wine; to this is to be added a bleaching liquor, made by dissolving pure carbonate of potash and then impregnating it with chlorine gas till the silica precipitates and the solution becomes slightly coloured. Of this bleaching liquor add 1 or 2 oz. to the spirituous solution of shellac and stir the whole well together. Effervescence takes place, and when this ceases add more of the

bleaching liquor, and thus proceed till the colour of the mixture has become pale. A second bleaching liquor is now to be added, made by diluting muriatic acid with thrice its bulk of water, and dropping into it pulverized red-lead till the last portions do not become white. Of this acid bleaching liquor small quantities at a time are to be added to the half-bleached shellac solution, allowing the effervescence, which takes place on each addition, to cease before a fresh portion is poured in. This is to be continued until the lac, now white, separates from the liquor. The supernatant fluid is now to be poured away, and the lac is to be well washed in repeated waters, and finally wrung as dry as possible in a cloth. The lac obtained in the foregoing process is to be dissolved in a pint of alcohol, more or less according to the required strength of the varnish, and after standing for some time in a gentle heat, the clear liquor, which is the varnish, is to be poured off from the sediment. Mr. Luning's process is as follows: Dissolve 5 oz. of shellac in a quart of rectified spirits of wine; boil for a few minutes with 10 oz. of well-burned and recently heated animal charcoal, when a small quantity of the solution should be drawn off and filtered; if not colourless a little more charcoal must be added. When all colour is removed press the liquor through silk, as linen absorbs more varnish, and afterwards filter it through fine blotting-paper. In cases where the wax found combined with the lac is objectionable, filter cold; if the wax be not injurious, filter hot. This kind of varnish should be used in a temperature of not less than 60° F.; it dries in a few minutes and is not liable to chill or bloom; it is therefore particularly applicable to drawings and prints which have been sized, and may be advantageously used upon oil paintings which have been painted a sufficient time, as it bears out colour with the purest effect. This quality prevents it from obscuring gilding, and renders it a valuable leather varnish to the bookbinder, to whose use it has been already applied with happy effect, and does not yield to the warmth of the hand, and resists damps, which subjects bindings to mildew. Its useful applications are very numerous, indeed to all the purposes of the best hard spirit varnishes, it is to be used under the same conditions and with the same management.

The essential requirements of a perfectly bleached shellac consist in the colour being transformed to the maximum degree of whiteness, while hardness and solubility must also be developed to the greatest possible extent. In European countries the process is carried out in a manner which would appear to leave no room for improvement, the desirable attributes being present in the finished product to a pronounced extent. The details of a critical examination by an American expert of several samples of bleached shellac imported from France, England, and Germany by a leading industrial chemist, herewith given, will doubtless prove interesting, alike to the practical varnish-maker and varnisher.

A comparative test, partaking of the nature of a chemical

analysis, was made of each sample, with the result that the French material outclassed the other varieties in the superiority of its whiteness, its property of successfully resisting atmospheric influences, and finally with regard to one of the most important features, its surpassing dissolving power. In this sample were comprised the three indispensable requirements of a faultless bleached shellac—whiteness, hardness, and solubility—the combination being admirably associated with each other in a manner which at once guaranteed permanence and the requisite working properties. The sample under investigation (French) was capable of withstanding a temperature of 90° F. without softening or presenting the objectionable "tacky" tendency characteristic of inferior products.

With regard to the question of hardness, the English variety exceeds the French, but the development of this especial feature involves certain operations in the treatment of the material which deleteriously affect other properties, the maximum development of which constitutes an important factor in a perfectly bleached shellac. Reference is here made especially to the property of solubility. It was found that the French product was much more susceptible of solution in alcohol and special menstrums than the English variety. Furthermore, a drawback coincident with the method of bleaching, as practised in case of the English sample, consists in the residue which forms as a result of solution.

This is the direct result of precipitating the shellac from a solution of hypochlorites of soda or potash by sulphuric acid, an insoluble residue of sulphate of lime settling at bottom.

The only practicable method yet discovered, by means of which the latter objection may be obviated, is by precipitating the bleached shellac from its alkaline solution by the use of an acid, which adequately neutralizes the solution without producing the residue. Diluted muriatic acid is the fluid which, in preference to sulphuric acid, has been found to produce the desired result referred to with regard to perfect solubility. In this respect the German sample proved satisfactory, and it is largely on the system which is carried on in Germany that the methods which are pursued in America are modelled.

In the highest standard of quality, considerable experience is necessary to master the complex system in its varying phases. To produce uniformity in the finished product, the operations, of which there are twelve, each distinctive and of equal importance, should be carried out with great precision, slowly and carefully.

The primary object in bleaching is to eliminate the insect colouring matter from the crude material, or button lac, by means of chemical treatment. A gum resin is thus produced, which, together with a suitable solvent, forms the colourless shellac varnish of commerce.

There are, however, further important functions devolving on certain of the operations other than that already specified. From

the crude material certain animal substances, exclusive of the colouring matter, must also be effectively eradicated, otherwise the desired end would be impracticable of accomplishment.

Much of the success of the operation depends upon the mechanical as well as upon the chemical treatment accorded the crude material and bleaching generally. By comparing American samples of bleached shellacs with the French materials the superiority of the latter becomes apparent. While the American product compares favourably with regard to colour for a brief period after having been treated, exposure to the air causes it to assume a yellowish aspect later on.

There is another defect which American bleached shellac at times presents, which is rarely if ever found in the foreign goods, and which consists in the propensity it displays to adhere to the barrel in which it is packed. This is owing to the increased temperature characteristic of summer weather, the action of which softens the material.

In shellac bleaching the operations, which are of a mechanical nature, exert a very important influence on the nature or general aspect and inherent properties of the finished product. That these operations should be carefully carried out is of peculiar significance to the varnish-maker who uses bleached shellac as an ingredient in the manufacture of spirit varnishes.

The twelve operations which are essential in shellac bleaching may be designated as follows :—

1. Crushing the raw material or button lac to a powder, so that it will become more easily soluble in the alkaline solution.
2. Separation of the colouring principle from the shellac.
3. Preparation of the bleaching agent, or hypochlorite of potash, or soda.
4. Treatment of the liquefied button lac by the bleaching agent.
5. Diluting the bleached shellac alkaline solution in water.
6. Preparing the sulphuric acid for neutralizing the alkaline solution of shellac.
7. Neutralizing the shellac alkaline solution by the use of diluted sulphuric acid, which coincidentally precipitates the bleached shellac.
8. Filtering the precipitate, or pulp, of white bleached shellac.
9. Malaxing the neutral pulp of bleached shellac to determine whiteness and elasticity.
10. Hardening and whitening process of the sulphuric acid bath, which prevents to a very great extent the white shellac from turning yellow when exposed to light.
11. Drying the bleached shellac.
12. Crushing the bleached shellac.

Chlorine acts very energetically, and often so modifies the resinous matter that it becomes altogether altered and unfit for use owing to its becoming very difficultly soluble in alcohol. Moreover, great

trouble is experienced in removing all the chlorine from the bleached shellac, even after repeated washing with water. The former afterwards acts injuriously when the resin is extended into a varnish, especially upon metals, and to such an extent as to exclude it from employment thereon.

Willstein's Process.—Five hundred parts of chloride of lime are mixed with 2000 parts of water, and a solution of 500 parts of carbonate of potash in 1500 parts of water is run in so long as a precipitate is formed. Into the filtered liquid there is run, a little at a time, a solution of 500 parts of orange shellac in 2000 parts of alcohol of 90 per cent strength. After the whole has been well stirred, it is allowed to stand, preferably in the sunlight. After half an hour to an hour the liquid containing the resin is run in a thin stream into dilute hydrochloric acid, 1 part of acid in parts of water. As soon as the resin is completely precipitated it is washed with water until free from acid. It is then churned with hot water until the latter is no longer coloured; finally, the hot resin is run into sticks, which are generally piled together. If the action of the chlorine has been too energetic, and if the shellac has been so altered as to become insoluble in alcohol, this may be remedied by breaking the shellac into small pieces and immersing these for twenty-four hours in ether, where it swells and is afterwards easily dissolved in alcohol.

Elsner's Method.—He uses animal charcoal to bleach shellac without altering it. He agitates an alcoholic solution of shellac with coarse-grained animal charcoal which has been previously washed with acid then with water and dried. The charcoal is made into paste with the alcohol solution, and the whole, when completely bleached in the sun, filtered and evaporated. But this method is very costly, and shellac evaporated from alcohol is quite altered in its properties.

Benedict's Process.—Forty lb. shellac are heated with a solution of 10 lb. of carbonate of soda in 15 gallons water until dissolved. The liquid, clarified by standing, is decanted into a filtered solution of 40 lb. of chloride of lime in water, leaving the whole to stand from twenty-four to forty-eight hours, and then precipitating the resin by hydrochloric acid as in the preceding method.

Alkaline Method without Chlorine.—Add shellac in small quantities to dilute boiling soda lye, taking care not to make a fresh addition until the previous lot has been dissolved, stopping short when there is a slight excess of free soda. When all is dissolved, boil for a few moments with constant stirring and then cool. The wax which solidifies on the surface is removed, and the liquid filtered if need be, to obtain a clear solution, which is treated with hydrochloric acid as before. But the product still contains an appreciable amount of colouring matter. Too long boiling with alkaline lye, even if very dilute, must be avoided, as the substance would be converted into a balsam of the same centesimal composition (Benedict's liquid lac). The HCl can be replaced by H_2SO_3.

Composition of Shellac.—Unverdorben found in shellac:—

1. A resin soluble in alcohol and ether.
2. A resin soluble in alcohol but not in ether.
3. A resin slightly soluble in cold alcohol.
4. A crystalline resin.
5. A wax.
6. Oleic and stearic acids.
7. A brown substance, which was termed laccine.
8. A red colouring matter.

TABLE LXXXII.—JOHN'S ANALYSIS OF SHELLAC.

	Per cent.
Resin, five resinoid bodies	66·55
Peculiar yellow substance, Lackstoff	16·70
Colouring matter	3·75
Extractive	3·92
Peculiar acid, laccic acid	0·62
Chitine	2·08
Waxy matter	1·67
Salts	1·04
Sand and earth	0·62

TABLE LXXXIII.—HATCHETT'S ANALYSIS OF SHELLAC.

	Stick Lac.	Seed Lac.	Shellac.
Resin	68·0	88·5	90·9
Colouring matter	10·0	2·5	0·5
Wax	6·0	4·5	4·0
Gluten	5·5	2·0	2·8
Foreign bodies	6·5	—	—
Loss	4·0	2·5	1·8
	100·0	100·0	100·0

TABLE LXXXIV.—HOOPER'S ANALYSIS OF SHELLAC FROM VARIOUS SOURCES.

Lac.	Tree.	Water.	Resins.	Colouring.	Residue.	Ash.
Kusum	Schleichera trijuga	1·8	85·6	2·5	9·1	1·0
Ficus	Ficus	1·8	88·9	2·6	10·2	1·5
Ber	Zizyphus Jujuba	2·0	82·7	2·4	11·5	1·8
Palas	Butea Frondosa	2·4	77·4	4·3	14·1	1·8

Kusum lac is evidently the purest. The iodine number of the crude lacs averaged 11·4 per cent. The residue, left after extraction of shellac from the crude lac, known as keri, still contains a large proportion of lac, amounting to 55 to 72 per cent, but this is reduced by a new method of extraction to 15·5 per cent. Probably the new method mentioned is that previously recommended by Hooper, i.e.

extraction of the lac by means of methylated spirit (see p. 299). According to Farner, stick lac contains 74·5 per cent of resinous matter, 6·0 per cent of wax, 6·5 per cent of colouring matter, 9·5 per cent of impurities, and 3·5 per cent of moisture, which is in substantial agreement with the figures above quoted.

Shellac wax was found by Benedict and Ulzer to contain both ceryl and myricyl alcohols in combination with both fatty and resinous acids. The saponification value of shellac wax was 57·6, and the acetyl derivative had a saponification value of 115. The wax thus contains about 50 per cent of these alcohols in the free state.

Benedict and Ulzer, by treating shellac with alcohol and ignited magnesia, prepared magnesium salts of the acids, which decomposed with dilute sulphuric acid and yielded a viscous mass. This, when dried, gave off water and formed a hard mass like the original shellac. This substance had the same elementary composition as shellac, but the acidity was much higher, e.g. 204·66. Its formula was $C_{46}H_{72}O_{12}$.

By oxidation of shellac by alkaline permanganate, they obtained azelaic acid ($C_7H_{14}(COOH)_2$), a dibasic acid, which is also a product of the unsaturated acids from drying oils when similarly treated.

TABLE LXXXV.—CONSTANTS OF SHELLAC.

	Acid Value.	Saponification Value.	Ether Value.	Iodine Value.
Medium (Schmidt and Erban)	65·1	213·3	148·2	8·30
„ (Williams)	63·0	203·3	140·3	24·62
Garnet „	56·0	212·6	156·6	28·70
Orange (Schmidt and Erban)	60·0	211·6	151·6	—
Good (Williams)	47·6	210·7	163·1	20·40
Light „	56·0	211·4	155·4	19·81
D.C. (Langmuir)	—	—	—	15·90
Good Ralli (Langmuir)	—	—	—	16·00
„ TN „	—	—	—	17·70
„ Button „	—	—	—	15·80
Not specified (Ulzer and Defries)	65·4	204·8	139·4	—
Stick lac (Ruder)	39·2	212·8	173·6	16·00
„ „	40·7	221·2	180·5	16·60
„ „	47·9	260·1	112·2	19·50
„ „	56·0	226·8	170·8	8·00
Seed lac „	53·0	218·4	165·4	7·50
„ „	54·5	224·2	169·7	8·70
„ „	61·1	251·9	190·8	8·60
„ „	56·0	224·0	168·0	3·60
Button lac „	58·8	204·4	145·6	22·20
„ „	60·0	208·5	148·5	22·60
„ „	61·9	215·2	153·3	23·30
„ „	64·0	212·8	148·8	19·00
Average	56·1	218·3	153·2	16·10

Storch-Morawski Reaction.—This well-known test for rosin in shellac depends on the red-violet colour produced on adding a drop of strong sulphuric acid to the solution of the shellac in acetic

anhydride. A little shellac is dissolved by gently warming with acetic anhydride, and a drop of sulphuric acid added to the cooled solution. A decided response is got with 10 per cent rosin, a doubtful one with 5 per cent. The following is one of the numerous modifications which it is claimed renders the test more sensitive: One gramme of the sample is treated with 15 c.c. of acetic anhydride. The mixture is gently warmed on the water-bath until solution is complete, and cooled by standing in cold water. Rosin remains in solution. The greater part of the shellac separates as a gelatinous mass, which is filtered off. In this way the rosin is concentrated in the filtrate. The test-tube is inclined, and a couple of drops of strong sulphuric acid allowed to flow down the side, agitating the liquid a little as the acid meets it. A coloration, which soon disappears, is obtained with as little as 2 or 3 per cent of rosin. A pure shellac gives no coloration if care has been taken to avoid charring.

In a paper on the "Commercial Grades of Lac and their Valuation," read before the Pharmaceutical Society of Great Britain, Mr. John C. Umney states that this test will reveal rosin adulteration in lac only above 7 per cent. Mr. A. Suter criticizes this statement. He disagrees, he says, "because, if the test is carefully and uniformly performed, it is certainly capable of producing positive results with as little as 2½ per cent of rosin present; check-analyses by theiodine absorption have convinced me of that. Indeed, I go further and state that with a large amount of practice the observer will be able to distinguish an absolutely rosin-free lac from one with an adulteration of less than 2½ per cent although no coloration is produced. For this purpose it is, however, necessary to use sulphuric acid of 1·53 specific gravity, which can be prepared by mixing 34·7 c.c. of conc. sulphuric acid with 37·5 c.c. of distilled water. By means of this test a rough grading of shellac into the following three groups could, with some experience, be effected:—

"(*a*) Lacs, producing no coloration. Inference—under 2½ per cent of resin. Good lacs.

"(*b*) Lacs, producing a fair amount of coloration. Inference—2½ to 5 per cent of rosin present. Fair lacs.

"(*c*) Lacs, producing an intense coloration. Inference—5 to 10 per cent of rosin present. Bad lacs."

It is unnecessary to quote further modifications. The writer has queried the use of anhydride instead of glacial acetic acid as originally used by Liebermann, and is told by Mr. C. Harrison of the Borough Polytechnic that the reaction succeeds better with glacial acetic in so far as it is not so transient.

The analysis of shellac resolves itself into a determination of the percentage of rosin present, if any. Hirschsohn's process consists in treating the shellac with petroleum ether, in which common rosin freely dissolves, whilst shellac is only very partially dissolved. Of eleven samples Hirschsohn found the solubility in petroleum ether to vary from 1·20 to 14·25 per cent.

The Petroleum Ether—Method of Estimating Rosin in Shellac.—This test is based on the following facts: Rosin is soluble in petroleum ether, so also is shellac wax, but shellac proper is insoluble. The different and contradictory results obtained by extracting shellac with petroleum ether by different observers, and by the same observer, are readily understood. Petroleum ether is not a definite chemical compound, and those who work with it omit the two important points, the only ones in fact that will give some clue to its nature, viz. its specific gravity and its boiling-point. Again, if rosin of itself be soluble in the so-called petroleum ether, it does not follow that no chemical action ensues when rosin is fused with shellac so as to render it more or less insoluble. Langmuir simply begs the question when he says: "A separation of a fused mixture of the two is practically impossible, however, as the insoluble shellac protects the rosin from solution". There is no data whatever to support his conclusion that when rosin and shellac are fused together they form nothing but a mere mechanical mixture or solution of the one in the other. No doubt the wax present in shellac is a disturbing element. Langmuir recommends the wax to be removed by dissolving the shellac in warm dilute carbonate of soda solution, cooling and filtering off the wax. Now there is nothing to show that in this style of working some of the rosin is not entrained by the wax. Again, Langmuir begs the question that rosin which has been treated with carbonate of soda and precipitated by acid retains its original solubility in petroleum spirit. But from the author's experience in dealing with petroleum spirit as a solvent for rosin and rosinates, he believes that rosin treated with carbonate of soda so as to dissolve it in water, and then precipitated therefrom, is far less soluble in petroleum spirit than the original rosin, and does not dissolve freely therein until the combined water precipitated with it has been expelled by heat. Langmuir goes on to say: "The shellac is thrown out of the filtrate (from the wax) by acid filtered on a Buchner filter, washed and dried. In this condition it is wax-free and in a very finely divided state, offering the most favourable chances for a successful extraction of rosin." But however fine the rosin is hydrated and thus less soluble in petrol, and in saponifying the rosin in shellac the operator is groping in the dark, the unsaponifiable wax masks any unsaponified rosin, and to apply Langmuir's own arguments, the insoluble wax protects the entrained rosin from solution, and moreover, but not only so, it hides it from the eye of the operator at the same time. Langmuir extracted 5 grammes of finely ground button lac in a Soxhlet for five hours, extract 5·07 per cent, largely wax. Five hours extra gave 0·48 per cent. The same button, purified as above, gave 1·55 per cent to the ether. This bears out the above criticisms; solution and precipitation had rendered the rosin insoluble in the petroleum ether. A pure button, freed from wax by Langmuir as above, gave 0·38 per cent soluble matter. Similarly, seven bleached shellacs of American

make were finely pulverized and passed through an 80-mesh sieve and 10 grammes extracted for five hours, giving 1·05, 1·08, 1·84, 1·75, 2·43, 4·23, and 4·30 per cent respectively. Here we again meet with the tacit assumption that the rosin in a chlorinated, or sulphited alkaline solution of shellac, is inert to the bleaching agent, and that the solubility of the rosin in petroleum is the same as in the case of rosin by itself. A pure bleached Ralli gave 3·35 per cent soluble. The residues from the evaporation of the ether were of a waxy character and showed no indications of rosin. Langmuir also examined a poor quality of TN, which he finely ground and extracted for five hours, but it only gave an extract of 1·6 per cent. A good TN gave 0·6 per cent. Langmuir got better results with freshly prepared artificial mixtures of rosin and shellac, but they were far from the truth. If the writer quite agrees with Langmuir that no safe inferences can be drawn from the results of a petroleum ether extraction, yet Langmuir, as will be seen, did not perhaps apply the test in the most rational manner; and his deductions seem to show that he fails to grasp all the issues involved and the possible reactions that might come into play. Langmuir criticizes the copper acetate test for rosin in shellac in these terms: "A published test for rosin is to shake the petroleum ether extract with a little water containing some copper acetate; the ether layer will be coloured emerald green if rosin is present. In our hands artificial mixtures of shellac and rosin failed to show the latter if less than 15 per cent were present." That is no doubt true; neither acetate nor rosinate of copper dissolves in petroleum spirit until the petroleum spirit has taken up a certain amount of free rosin. See Vol. II. of this treatise (p. 164), where a saturated solution of rosin in naphtha is used to dissolve copper rosinate.

If Langmuir did not succeed with petroleum ether, McIlheny by applying this test in a more rational and in a quantitative separation manner seems to have met with well-deserved success. The question is so important that his method is given here at some length. McIlheny shows at the very outset that he has grasped the points at issue by his prefatory remarks:—

"Several experimenters have attempted to separate rosin from shellac by taking advantage of the solubility of rosin in petroleum ether, a solvent in which shellac is insoluble. No method of extracting from even a finely pulverized sample of shellac the portion soluble in petroleum ether seems to be capable of removing more than a small part of the rosin contained in the sample.

"Shellac dissolves in alcohol, except for the wax contained in it; petroleum ether dissolves to some extent in alcohol, and it was thought that by first dissolving the shellac to be analysed in alcohol, then adding to the solution all the petroleum ether which it would dissolve and then adding water, so as to so dilute the alcohol that it would no longer have any material solvent power upon either rosin or shellac, there should result a separation of the dissolved

petroleum ether containing in solution the rosin and the wax, but free from the resinous constituents of the shellac. Upon trying that process, it appeared that it was correct in principle, but on account of the limited solubility of petroleum ether in alcohol the separation was not quite complete. Upon substituting for ordinary alcohol, glacial acetic acid, or absolute alcohol, in which the sample of shellac to be examined is dissolved, and then adding to it petroleum ether, which is miscible in all proportions with acetic acid, or absolute alcohol, it was found practicable to combine with the rosin and the wax so large an amount of petroleum ether that, upon adding water, an almost complete separation of the rosin and wax from the resinous part of the shellac could be effected."

Based upon these facts, the following process was devised: Dissolve in 20 c.c. of glacial acetic acid (about 99 per cent) or the same volume of absolute alcohol, 2 grammes of the sample to be analysed. This requires a gentle heat. Add to the solution, after cooling, 100 to 300 c.c. of petroleum ether, boiling under 80° C. This addition of petroleum ether should be made slowly, because so large an amount precipitates from its solution a part of the shellac, combined, apparently, in case acetic acid was the original solvent, with acetic acid to form a liquid precipitate. It is manifestly desirable that this precipitation of part of the shellac should not be effected by too sudden an addition of petroleum ether, as it might then contain some rosin carried down mechanically with it.

We now have a solution containing both petroleum ether and glacial acetic acid, or absolute alcohol, and containing in it, in solution, all the rosin, all the wax, and most of the resinous part of the shellac. Add now to this solution, drop by drop, 100 c.c. of water, agitating the liquid during the addition. The water "unites with" the alcohol or acetic acid, and separates from the liquid the petroleum ether with whatever is soluble in petroleum ether. This includes the rosin and the wax. The shellac is also precipitated, but as it is insoluble in petroleum ether it remains as a precipitate suspended in the diluted alcohol or acetic acid. The separation of the two liquids takes place very rapidly, and it is an easy matter to effect a complete separation of the two layers in a separating funnel. The petroleum ether layer is washed once or twice with water, and then filtered through a dry paper into a weighed flask, from which the petroleum ether is then distilled off, leaving the residue of rosin mixed with wax, which is weighed. To the weighed residue neutral alcohol is added, and the flask heated to dissolve the rosin in the alcohol. The liquid is then titrated with N/5 or N/10 caustic potash. This gives a measure of the amount of rosin present, as the average combining equivalent of rosin does not vary greatly from 346. This is the figure used for this titration in the Twitchell process. It is much better, however, not to depend upon his determination of the rosin, but to proceed to an actual separation by adding to the neutralized alcoholic solution a distinct excess of alkali and a sufficient

quantity of petroleum ether; the mixture is then transferred to a separating funnel, thoroughly agitated, and some water added. The liquids are then separated, the petroleum ether layer being washed with water, and the alcoholic solution of the rosin extracted once more with petroleum ether. The petroleum ether solutions are then united, the petroleum ether distilled off, and the residue of wax weighed. The alcoholic solution containing the rosin is then boiled until the alcohol has been expelled, and, if necessary, a further addition of water made; then dilute hydrochloric acid is added, so as to precipitate the rosin. This should be done in a weighed flask; the acidified liquid can now be decanted off through a wet filter-paper, so as to leave behind in the flask the major part of the rosin, which is washed with water. The remainder of the rosin upon the filter paper, after sufficient washing, is extracted with petroleum ether back into the weighed flask from which the water has been decanted as perfectly as possible. Upon distilling off the petroleum ether, the rosin is left behind in a condition to weigh. If the whole of the last traces of water have not been removed by the distillation with petroleum ether, it is well to add a further quantity of dry petroleum ether and distil again. Attempts were made to use other solvents, particularly coal-tar benzene instead of petroleum ether. It was found, however, that benzene dissolved considerably more out of the shellac than the wax.

If it is desired to determine only the rosin in the shellac, it is unnecessary to distil off all the petroleum ether from the solution containing the wax and the rosin. This solution may, instead, be treated directly with an alkali capable of combining with the rosin, while leaving the wax unattacked. The most convenient method McIlheny found for accomplishing this is to add to the petroleum ether solution, after filtering it to remove from it anything which it may contain in suspension, a solution of sodium hydroxide in absolute alcohol. Such a solution is made by dissolving in ordinary 95 per cent alcohol the appropriate amount of metallic sodium.[1] When added to the petroleum ether solution, it mixes perfectly and the alkali combines with the rosin, and the mixed solution allows the saponified rosin to be extracted from it by agitation with water, or, better, with slightly diluted alcohol. Instead of using a solution of sodium hydroxide in absolute alcohol, it should be possible to use the method of separating rosin from neutral substances in petroleum ether solution that is used in the Twitchell process of determining rosin in admixture with fatty acid. This consists in agitating the petroleum ether solution with an alkaline aqueous solution containing some alcohol, made by dissolving 1 gramme of potassium hydroxide with 10 c.c. of alcohol in water, and diluting to 100 c.c. The other method of procedure is advantageous, however, and gives a more exact separation. The solution drawn off from the petroleum

[1] The result of the action of sodium on alcohol is generally regarded as sodium *ethylate* (sodium ethoxide).

ether, after extraction by alkali, and containing in solution the rosin combined with potassium or sodium, together with whatever alcohol has been used to promote the combination and to facilitate the mechanical separation of the two liquids, is heated for some time to remove the alcohol, and is then acidified with hydrochloric or with sulphuric acid to precipitate the rosin. The precipitated rosin is then weighed as before.

Without entering into a discussion of the exact chemical composition of shellac wax, it may be proper to state that the wax may be separated commercially from shellac by two essentially different methods, which will probably give waxes having somewhat different compositions. If the shellac is dissolved in an alkaline solution and the wax which remains in suspension is filtered out, it is probable that different results will be obtained from what would be obtained by the other process, consisting of a solution of the shellac in alcohol, and filtration of the solution to remove the wax which will remain in suspension. It is to be expected that these two processes of solution would leave, in the undissolved wax, small amounts of ingredients of different characters, and, furthermore, the alcohol used in the second process would dissolve small amounts of the wax which would probably be quite insoluble in an alkaline aqueous solution. Again, it is quite probable that a caustic solution would behave towards shellac wax somewhat differently from a dilute carbonate solution. For the sake of uniformity and simplicity, McIlheny assumes that shellac wax is quite free, when pure, from all acid substances capable of uniting with free alkali. It is nevertheless true that the user of shellac who wishes to have a determination made of the amount of wax which it contains usually desires this information in order that he may know how much of the shellac will remain undissolved in alcohol. This amount of insoluble wax varies with the strength of the varnish that he prepares with it; that is to say, the number of pounds of shellac which he uses to a gallon of alcohol. As the analyst can hardly be expected to take account of this in making his test, it appears more rational to regard as wax the whole of those matters contained in the shellac that remain insoluble in an alkaline solution.

In determining the wax, it is to be observed that some constituent of shellac wax is only difficultly soluble in petroleum ether. On analysing several portions of the same lot of shellac, the only difference made being that varying amounts of petroleum ether were used, increasing amounts of petroleum ether gave increasing percentages of wax, until the proportion of about 125 to 150 c.c. of the solvent to 1 gramme of a shellac containing about 5 per cent of wax was reached. By using some other solvent such as benzine, a smaller amount may suffice, but as it seldom happens that only wax without rosin is to be determined, petroleum ether is the most generally applicable solvent. The solubility of rosin in petroleum ether is so easy and complete that no difficulty is experienced in extracting

from 2 grammes of shellac 50 per cent of rosin, using 100 c.c. of petroleum ether.

On acidifying the aqueous solution which should contain the rosin, the identity of the separated matter may be established by determining its iodine figure by the Langmuir method, and its acidity by titrating with alkali in alcoholic solution.

The petroleum ether referred to here is a solvent made by re-distilling 0·702 benzine, separating for use that part which distils below 80° C. This fraction constitutes a large proportion of 0·702 benzine, and such a re-distillation gives, at a comparatively small cost, a satisfactory solvent for the purpose. If a determination of only the rosin is desired, it is, of course, unnecessary to be very particular as to the volatility of the solvent used, as it is unnecessary in such case to distil it off before extracting the rosin by alkali.

By treating pure shellac it is possible to separate from it a small amount, sometimes as much as 1 per cent, of materials soluble in petroleum ether. This small amount of resinous matter, when examined, proves to be something essentially different from common rosin. Its odour and its low iodine figure indicate that it is some resinous constituent of shellac, perhaps a small amount of the major constituent, which is slightly soluble in petroleum ether. As it is difficult to imagine that by this process rosin if a normal constituent of pure shellac would escape detection, and as the small amount of resinous matter here obtained is essentially different from rosin, it is reasonable to conclude that, contrary to the idea held by many, common rosin, or a material similar to it, is not a natural constituent of pure shellac, but that any rosin or colophony which can be separated in a state of reasonable purity from the sample of shellac was originally added to the shellac as an adulterant.

The process here described allows the analyst to separate in a form convenient for exhibition either as evidence in court or as an ocular demonstration for his client any rosin which may have been added as an adulterant to shellac.

Shellac varnishes may contain besides true shellac not only rosin, but other gums and resins soluble in alcohol. It becomes therefore a matter of interest to ascertain how some of these other resins behave when treated by this process. Two samples of Manila, when treated, using absolute alcohol as the first solvent, gave, respectively, 41·2 and 43·3 per cent of matter soluble in petroleum ether. The acidity of these two lots of matter soluble in petroleum ether was in the case of the first sample such that 1 c.c. of normal alkali neutralized 411·7 milligrammes, and in the case of the second 470·7 milligrammes. Two samples of kauri gave, respectively, 37·9 and 27·0 per cent. Upon titrating with standard alkali these portions soluble in petroleum ether, it appeared that 1 c.c. of normal alkali was capable of neutralizing 903·6 milligrammes and 724·5 milligrammes respectively. Of sandarach, two samples, when similarly analysed, gave 34·96 and 36·19 per cent, having such an

acidity that of the first 541·2 milligrammes would neutralize 1 c.c. normal alkali, and of the second 552·5 milligrammes would neutralize 1 c.c. Of dammar, 89·9 per cent proved to be soluble, while the resin of *Shorea robusta*, a sample of which was kindly sent by Mr. W. Risdon Criper, of Calcutta, gave 69·5 per cent of soluble matter. [Yet *Shorea robusta* is a host of the shellac insect!]

A number of attempts were made to effect a satisfactory separation of the wax before separating the rosin from the shellac. It was found, however, that on account of the solubility of wax in alcohol and in glacial acetic acid, this separation could not well be made by filtering out the wax before the addition of petroleum ether. Neither were attempts which were made to separate the wax by a preliminary solution of the shellac in aqueous alkali successful in furnishing a method that at all approached in feasibility to the method already described.

The Detection of Rosin in Shellac by the Determination of the Iodine Value.—One of the methods for determining rosin in shellac is based on the different capacities of rosin and shellac to absorb iodine when presented to a solution of the shellac in an appropriate manner. All the methods are said to give fair results. But it must be borne in mind that some of the hosts of the shellac insect, for instance *Shorea robusta*, secrete resin in the case of the latter black dammar. Now as the twigs, etc., of the latter tree must contain dammar, and that dammar, by the crushing of the twigs, etc., must of necessity enter the shellac, no hard and fast rules as to the iodine value of shellac can very well be applied, the more so as some shellac is boiled with caustic or carbonated alkali to remove the dye and other kinds are not. But if both kinds are equally genuine, yet it is irrational to expect them to agree in a hard and fast way as to their iodine value. As Langmuir's application of Wijs' method is as reliable a method of determining the iodine value as any of the numerous variations of the Hübl method, it will be well to give it at some length.

If, says Langmuir, Wijs' solution, rather than Hübl's, be used in the test for rosin, there is the great advantage that a qualitative reaction is furnished, simultaneously with the quantitative determination. Furthermore, if the details to be given are followed, a higher number for rosin is obtained than heretofore, and the difference between the absorption of rosin and that of shellac is so great that a very satisfactory basis for calculation is furnished, and the method gains greatly in sensitiveness and accuracy. Shellac stands alone among the resins in its low iodine absorption. Rosin has an uncommonly high absorption. Ingle states that "all ordinary oils merely reduce the intensity of shade of Wijs' solution by absorption of iodine chloride. Boiled and blown oils colour Wijs' solution red-brown." Shellac has no effect on the colour of Wijs' solution (except after long standing); rosin, even when mixed with shellac in small amount, speedily produces a characteristic red-brown colora-

tion in proportion to the quantity present. By comparison with artificial samples, containing known proportions of shellac and rosin, a fair colorimetric estimation can be made. There is no trouble whatever in preparing the Wijs' solution. It is more active than the Hanaus solution, and a smaller excess is required. The use of the latter should be discouraged as tending to a troublesome duplication of data. Four litres at a time is prepared. Glacial acetic acid is used. The acid should always be tested for reducing impurities; 51 grammes of finely divided iodine is dissolved at a gentle heat. A portion of about 250 c.c. is set aside; 20 c.c. is taken for titration. Suppose 20·7 c.c. of sodium thiosulphate solution are required. Pure chlorine is passed into the remaining solution until the characteristic colour change takes place; 20 c.c. of this are titrated. Suppose the amount required to be 41·7 c.c. The unchlorinated portion is now added until the titer is reduced to 0·1 or 0·2 c.c. less than 2 × 20·7 c.c. or 41·4 c.c. The deci-normal sodium thiosulphate solution is best standardized directly against iodine, sublimed from a tube containing a mixture of iodine with 20 per cent of potassium iodide into a weighing bottle 6·5 × 1·5 cm. diameter. The first vapours are rejected. After weighing the iodine is dissolved in strong potassium iodide solution, and shaken up in the weighing bottle.

Langmuir's Method.—0·2 grammes of ground shellac is introduced into a 250 c.c. bottle with ground stopper; 20 c.c. of glacial acetic acid is added, and the mixture warmed gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble. Solution is quicker according to the proportion of rosin present; 10 c.c. of chloroform is added, and the solution is cooled to 21° to 24° C. The temperature should be held between these limits during the test. The colour at this stage is a light yellow. Little difference is noticeable between shellacs, the lac dye having little effect; 20 c.c. of Wijs' solution is added from a pipette, the end of which has been heated to diminish somewhat the size of the orifice. The bottle is closed and the time noted. The solution is stood in a dark place. Pure shellacs will scarcely alter the colour of the Wijs' solution. A small amount of rosin will produce a slowly appearing red-brown colour. A large amount of rosin causes an immediate coloration, increasing in intensity as time passes. After one hour 10 c.c. of 10 per cent potassium iodide solution is added. The solution is immediately titrated with $N/_{10}$ thiosulphate solution; 25 c.c. or 30 c.c. may be run in immediately, unless the shellac is very impure, and the remainder gradually, with vigorous shaking. Just before the end a little starch solution is added. The end point is sharp, as the reaction products of shellac remain dissolved in the chloroform. Any colour remaining after a half-minute or so is disregarded. A blank determination should be run with 20 c.c. of Wijs' solution, 20 c.c. of acetic acid, and 10 c.c. of chloroform. The blank is necessary on account of the well-known effect of temperature changes on the volume.

Example :—
Ralli shellac 0·2 gramme.
Blank 20 c.c. Wijs' solution 41·1 c.c. hypo. 1 c.c. = ·0123 I
Required in test 35·6 ,, ,,

Equiv. to iodine absorbed 5·5 ,, ,,
$5·5 \times 100 \times ·0123 \div ·2 = 33·9$ per cent iodine absorbed.

In testing rosin, 0·15 gramme with 20 c.c. acetic acid, 10 c.c. chloroform, and 40 c.c. Wijs' solution is used, the other conditions as to time and temperature remaining exactly as with shellac. With bleached shellacs 0·4 gramme is taken, other conditions remaining unchanged.

Effect of Dirt, Orpiment, Wood, etc.—The only effect noticed was due to the lowering of the iodine absorption by the presence of extraneous matter, less shellac being present to absorb iodine. Except in very dirty samples this error is negligible. Time is an important factor, as the following experiments show. Conditions were precisely as given in the method above, except for the variation in time.

TABLE LXXXVI.—SHOWING EFFECT OF THE ELEMENT OF TIME IN IODINE ABSORPTIONS OF BUTTON LACS AND ROSINS (LANGMUIR).

Time. Hour.	Iodine Absorption.		
	Pure Button Lac. Per cent.	Light Rosin "M". Per cent.	"WW" Rosin. Per cent.
½	8·3	222·3	—
1	16·0	233·4	250
2	17·2	253·0	—
3	18·5	252·0	279·1

Influence of Temperature.—Other factors remaining unchanged, the temperature was varied ; time, one hour.

TABLE LXXXVII.—SHOWING EFFECT OF TEMPERATURE ON IODINE ABSORPTIONS OF BUTTON LACS AND ROSINS (LANGMUIR).

Temperature. ° C.	Iodine Absorption.	
	Pure Button Lac. Per cent.	Light Rosin "M". Per cent.
12	10·8	209·5
22	16·6	235·0
33	22·4	265·6

The shellac and rosin used in each series are the same. The agreement between the respective rosin and shellac values is note-

worthy in the two series where the conditions are identical—i.e. shellac, 16·0 and 16·6; rosin, 233·4 and 235·0.

Excess of Wijs' Solution.—No experiments were made, a liberal excess being used in all tests. *Effect of Light.*—No experiments were made in direct sunlight. Comparative tests on shellac and rosin showed no differences between darkness and moderate light lying outside of experimental errors. *Effect of Shellac Wax.*—The wax has an absorption of only 4·5 per cent, and can be disregarded.

An examination of the above results is convincing as to the necessity for keeping the time and temperature constant. If these conditions are observed, concordant results can invariably be obtained on well-mixed samples. Duplicates will not agree as closely as those obtained with non-drying oils, but on account of the enormous difference in iodine absorption between shellac and rosin, a slight variation in the iodine value between duplicates it is urged is of little consequence.

Iodine Absorption of Shellac.—A series of standard samples of shellac obtained from a well-known firm gave iodine absorption values of 16·0, 15·4, 16·0, 13·5, 15·1, 19·7, 21·5, 14·8, 17·2, 18·5, 16·0, 31·4, 15·4, 15·4, and 26·5. The following samples of pure shellac were drawn from cases or large lots:—

TABLE LXXXVIII.—IODINE ABSORPTION OF COMMERCIAL SHELLAC (LANGMUIR).

Shellac.	Iodine Absorption. Per cent.
DC	15·9
Good Ralli	16·0
„ TN	17·7
„ Button (year 1897)	15·8

Many other analyses of shellacs, which have bleached well and gave no evidence of rosin in any way, gave iodine values of 18 or less. After a consideration of the iodine values of the better grades of standards and the others given, it must be admitted that it is perfectly fair to take as the iodine number of a shellac free from rosin the number 18. If anything, this value favours the dealer, for an absolutely rosin-free shellac undoubtedly has a value below this. Roughly speaking, it could be said that a shellac with a value 18 or less would be a good shellac. Such a shellac will give good results when used; 18 to 23 would be a fair shellac. At 23 various qualitative tests for rosin begin to reveal its presence; 23 to 28 would indicate a poor shellac; 28 to 33 bad. A shellac above 33 is grossly adulterated.

Iodine Absorption of Rosin.—Various rosins show considerable differences in their ability to absorb iodine. The samples are of American origin only:—

TABLE LXXXIX.—IODINE ABSORPTION OF VARIOUS BRANDS OF ROSIN.

Rosin.	Iodine Absorption. Per cent.
"M"	235
WW 1	262·5
„ 2	228·4
„ 3	244·6
„ 4	224·3
„ 5	217·5
H 1	233
„ 2	225·6
Dark 1	175·7
„ 2	178

The light-coloured, soft varieties of rosin would probably have the highest iodine values, as they contain more residual turpentine after the distillation of the latter.

Calculation of the Percentage of Rosin.—In all probability, light rosins are used in the adulteration of button lac. A small piece of rosin found in a case of button was of the light variety, and had an iodine absorption of 202. In another case, part of a stave from a rosin barrel which had contained light rosin was found. In determining the rosin in button lac, a value for rosin well above 200 should be taken. The average of a number of tests on light rosins was 228, and Langmuir takes this figure as representing a fair average absorption for rosin. The darker-coloured shellacs, Ralli and TN, are probably adulterated with the cheaper dark rosins. The "Agricultural Ledger," No. 9, 1901, states that a common grade of American rosin is used in adulterating shellac. The average absorption of such rosins would probably be below 200. On account of the uncertainty, Langmuir preferred to take as a basis in calculating the per cent of rosin the value 228 for all shellacs, low or high grades. The results are probably closer to the truth in button lacs than in Ralli and TN. By taking the number as high as 228, however, no injustice can be done to the dealer, as any error would be in the direction of low results for rosin. The use of metallic rosinates, ester gums, glycerin-rosin compounds, etc., is very unlikely on account of their expense. Metallic compounds would reveal themselves in the ash of the shellac. Analyses of ash from various crude shellacs reveal nothing of this nature. Furthermore, no rosin preparation can be used in which the rosin has lost its solubility in alcohol. Such preparations have a lower iodine value than rosin itself. Any manipulation of the rosin, such as long exposure, heating, etc., would result in a lowering of the iodine absorption due to oxidation. A "WG" rosin, iodine absorption 226, was pulverized and spread out on glazed paper. After three weeks the iodine value had dropped to 193. If Y = per cent rosin, M = iodine number of shellac, N = iodine number of rosin, A = iodine number of mixture,

$$\text{Then } Y = \frac{100\,(A - M)}{N - M}$$

Taking the iodine numbers of shellac and rosin at 18 and 228 respectively, we have in the case of a TN shellac giving a number of 33·9 :—

$$\text{Per cent rosin} = \frac{100\,(33\cdot9 - 18)}{228 - 18} = 7\cdot6.$$

If a rosin of 190 value had been used we should have 9·2 per cent rosin. It is safe to say, therefore, that in the above case we are certain that there is at least 7·6 per cent rosin present. The following tables, based on the values, shellac 18, rosin 228, will give an idea of the relation between iodine absorption and per cent rosin :—

TABLE XC.—RELATION BETWEEN IODINE VALUE OF SHELLAC PER CENT AND ROSIN PER CENT PRESENT THEREIN (LANGMUIR).

Iodine Value.	Rosin. Per Cent.	Iodine Value.	Rosin. Per Cent.	Iodine Value.	Rosin. Per Cent.	Iodine Value.	Rosin. Per Cent.	Iodine Value.	Rosin. Per Cent.
18·00	—	39·0	10·0	60·0	20·0	81·0	30·0	102·0	40
23·25	2·5	44·25	12·5	65·25	22·5	86·25	32·5		
28·5	5·0	49·5	15·0	70·5	25·0	91·5	35·0		
33·75	7·5	54·75	17·5	75·75	27·5	96·75	37·5		

Extent of Adulteration.—The following results were obtained on samples taken from large lots of TN and Ralli shellac recently landed at New York.

TABLE XCI.—APPLICATION OF TABLE XC TO ESTIMATION OF SHELLAC (LANGMUIR).

Shellac.	Iodine Number.	Rosin. Per Cent.	Shellac.	Iodine Number.	Rosin. Per Cent.
Ralli, free . .	26·5	4·0	TN, free . .	22·9	2·3
" " . .	31·4	6·4	" blocked . .	27·3	4·4
" " . .	28·7	5·1	Ralli, free . .	19·7	0·8
TN, " . .	35·7	8·4	" " . .	15·9	—
" blocked . .	40·1	10·5	TN " . .	17·2	—
" " . .	42·7	11·8	" " . .	16·6	—
" " . .	30·6	6·0	" " . .	15·4	—
TN, matted . .	48·9	14·7	Ralli, blocked .	33·8	7·5
" blocked . .	63·0	21·4			

The tests given were taken at random from a large number. The rosin-free shellacs are in a decided minority, and the extent of adulteration shown is deplorable. Any shellac will block if the temperature is high enough, and a blocked article is not necessarily adulterated. Rosin, however, facilitates blocking by lowering the melting-point, and there is no doubt of the increase in blocked goods of late. The adulteration practised with TN and Ralli is far surpassed in the case of button lacs. With the exception of one brand, not a single sample of genuine button has been met with in the past year.

TABLE XCII.—SHOWING ROSIN CONTENT OF BUTTON LAC CALCULATED FROM IODINE VALUE (LANGMUIR).

Button Lac.	Iodine Number.	Per cent Rosin.
Ruby	73·6	26·5
Sapphire	70·4	25·0
Amethyst	77·4	28·3
Turquoise	68·5	24·0
Special	85·5	32·2

The average of thirty samples of button gave 57·8 iodine absorption = 18·9 per cent rosin.

As a check, a series of melts of button lac and rosin were made. One hundred gramme portions were cautiously melted on the sand-bath. The loss was 1·25 to 1·50 per cent. The results show that melting rosin and shellac together at moderate temperatures has no effect on the iodine absorption.

TABLE XCIII.—SHOWING ACTUAL ROSIN IN MELTS OF BUTTON LAC, AND ROSIN AND PERCENTAGE CALCULATED FROM IODINE VALUE (LANGMUIR).

	I. Button Lac 22·9. Dark Rosin 178.		II. Button Lac 20·7. Light Rosin 264 3.		Button Lac 16·2. Light Rosin 223·9.	
Rosin. Per cent.	Iodine Value.	Rosin Found. Per cent.	Iodine Value.	Rosin Found. Per cent.	Iodine Value.	Rosin Found. Per cent.
3	—	—	—	—	23·7	3·6
5	—	—	—	—	26·2	4·8
10	40·8	11·5	45·1	10·0	38·65	10·8
15	—	—	—	—	48·0	15·3
20	56·7	21·8	65·8	18·5	—	—
20	—	—	66·6	18·8	—	—
30	69·8	30·0	—	—	—	—

Even 3 per cent rosin increases iodine value from 16·2 to 23·7.

Physical Properties.—Colour is some guide to purity, but unsafe for Ralli and TN, and no guide for button lacs. In powdering shellac rosin shown by stickiness, a pure sample becomes strongly electrical in a coffee mill. Pure shellac can be pared with a knife without splintering. When crunched between the fingers and palms of the hand, adulterated shellac breaks readily into tiny pieces.

CHAPTER XX.

COLOURS AND STAINS.

Red Sanders.—There are three kinds of sandalwood, viz. white, yellow, and red. It is the wood of the latter variety, the *Pterocarpus santalinus*, the red sanders wood (*Lignum santali rubrum*), that is used in varnish staining. It is a solid, compact, dull, heavy, red-coloured wood imported from the Coromandel Coast and the mountainous parts of India. It is a small tree of South India, chiefly in Cuddapah, North Arcot, and the southern portion of the Carnul district. On a small area near Kodur in Cuddapah it has been very successfully cultivated. In former years the great use of the wood of this tree was as a dye, and large shipments were annually made from Madras to Europe, where it was employed as a colouring agent in pharmacy, for dyeing leather, and for staining wood. The demand, however, has now declined owing to the introduction of coal-tar dyes. In India the dye of red sanders is chiefly used in making idols and for staining the forehead in certain caste markings. The value of the wood as a dye is due to a red colouring principle, santaline, soluble in alcohol and ether but not in water. When dissolved in alcohol it dyes cloth a beautiful salmon pink. Its tincture is a fine spirit stain.

Santaline.—The chief colouring principle, which is very permanent, is santaline. It is present to the extent of 16·75 per cent ; it is a crystalline red powder melting a little below 212° F., soluble in alcohol, ether, acetic acid, and caustic alkalis. It may be extracted and isolated from the wood as follows: The finely powdered sandalwood is completely exhausted with alcohol and the alcoholic solution treated with an excess of hydrated oxide of lead (made by precipitating sugar of lead by caustic soda). The precipitate is collected on a filter, washed with alcohol, and dissolved in acetic acid. To the solution an excess of water is added which precipitates the colouring matter. The solution of acetate of lead may be used to make new hydrate of lead. The precipitated colouring principle, pure santaline, is washed and dried at a low temperature. In beauty and brightness it is nearly equal to carmine, and is of great interest to painters, who find it to be a very solid and fast colour. The carriages of Napoleon III were painted with it, and nine years afterwards were as bright as when first put on. Some authorities, however, describe it as fugitive, but that may possibly be due to the fact that the pigment was used in an alcoholic solution

Adulterations.—The powder is said to be frequently adulterated with red raddle, a fraud which may be detected by triturating 2 of the powder with 10 of water, and afterwards shaking with chloroform. The wood floats on the chloroform.

Safflower, or Carthamus tinctoria.—Bastard saffron is an annual plant, cultivated originally in the Levant, but afterwards in Persia, which furnishes the best quality, and other parts of Asia, Egypt, America, and Europe. There are several varieties of it, some with large, soft, almost non-spinose edible leaves, others with small,

FIG. 41.—*Bixa Orellana* (the source of annatto). Flowering branch and fruit.

very hard spinose leaves (*C. oxycanthe*). The latter is grown fairly extensively for its flowers, the safflower dye of commerce, but these conditions recur again, so no true characters can be given. The day's collection is carried to the homestead and partially dried in the shade, rubbed between hands, put on basket filters, and pure stream water run on to remove the soluble yellow dye. When the water is clear the florets are partially dried and pressed. Safflower cakes gunerat are sold in Bombay at 2 to 2½ lb. per rupee. Safflower seed, prized for its oil used in Afridi waxcloth, is the chief oil-seed crop of Bombay. It might be used here as a linseed oil substitute.

Composition.—Safflower contains two colouring principles, one yellow, the other red. The yellow principle is alone soluble in water.

Its solution is always turbid, giving with reagents the precipitates common to yellow colouring matters. The alkalis render it lighter, the acids deepen it in shade, giving it more of an orange hue ; both produce a small dun precipitate which clarifies it. Alum gives a slight deep yellow precipitate. The precipitates with the solution and other metallic salts are not characteristic. Alcohol takes but a slight dye out of those flowers from which the yellow substance has been previously extracted with water. But such flowers yield a yellow liquor, with caustic alkaline solutions, which on neutralizing with acid becomes turbid and reddish, and deposits a slight reddish-yellowish precipitate. Solutions of alum, zinc, and tin yield a yellow and those of iron a copper-greenish tinted precipitate. If a carbonate of an alkali has been used, the acids produce an abundant and a redder precipitate, but the shade differs according to the acid employed. Alum gives with the carbonated alkaline solution a red precipitate, which is so light that it usually floats on the surface of the liquor. This colouring matter is so delicate that it must not be treated with hot solutions, otherwise the precipitates have no longer the same beautiful colour. The petals of safflower have a fine flame colour. It should be gathered only when it begins to fade ; and it is better when it has received rain in this state, although there is a prejudice to the contrary. The rain may be supplied by an artificial watering of the flowers morning and evening. The seeds may still be left to ripen after the blossom is cropped.

These directions are given with the view of separating the yellow substance, a redundance of which may constitute the difference between the carthamus of Western Europe and that of the Levant. It is proper to keep the carthamus in a moist place, for too much drying might injure it. It has been grown successfully at Gottingen and Amiens. The yellow matter of safflower is not used, but in order to extract this portion the carthamus is put into a bag which is trodden under water till no more colour can be pressed out. The flowers which were yellow become reddish and lose nearly one-half in weight. These are now treated with alcohol, which extracts almost pure carthamine, a substance which is soluble in fatty oils, yielding a rose-red or orange-red liquid. According to Guignet, carthamine is very dear, rising as high as 3000 francs the kilogramme, but it has great tinctorial powers. It is extensively used in the preparation of vegetable rouge, which has the advantage of colouring the skin without dyeing it.

Annatto is a somewhat dry, hard paste, brown without and red within. It is usually imported in cakes of two or three pounds weight, wrapped up in leaves of large reeds, packed in casks from America, where it is prepared from the seeds of the *Bixa orellana* of Linnæus, the *Rocouyer* of the French. The pods of the tree being gathered their seeds are taken out and bruised, and it is from the resinoid pulp that the annatto is produced. They are now transferred to a vat, covered with water, and left for several weeks

or even months. The substance is now squeezed through a sieve placed over the vat so that the water containing the colouring matter may return thereto. The residue is covered with banana leaves and allowed to ferment, after which the process is repeated, and so on till no more colour remains. The substance thus extracted is passed through sieves to separate the remaining seeds and the colour is allowed to subside. The precipitate is boiled in coppers till reduced to a consistent paste; it is then suffered to cool and dried in the shade. Another and simpler method consists in simply washing the seeds of annatto until they are entirely deprived of their colour, which lies wholly on the surface, and precipitating the colouring principle by lemon juice or vinegar, and to boil down or to drain in bags. The annatto produced in this way is of quadruple value to that made by the previous process ; moreover, it dissolves more readily and gives a purer colour. Annatto contains two colouring principles, viz. orelline and bixine. Orelline is yellow, soluble in water and alcohol, and almost insoluble in ether, whilst bixine is red, very slightly soluble in water, but soluble in alcohol, ether, and alkaline solutions. According to Dr. John, annatto contains an aroma, an acid, resin combined with the colouring matter, vegetable mucilage fibrine, coloured extractive, and a peculiar matter which approaches to mucilage and extractive. This analysis explains why an alkali is added to annatto when used in drying. The alkali combines with the resin and forms a soap which dissolves in water. It likewise acts on the colouring matter, rendering it more lively. Annatto is often adulterated by sprinkling and mixing it with urine, which can be recognized by the smell of ammonia which it gives off when heated with caustic soda. It is sophisticated with ochre and sand, which are recognized on treating with alcohol. A decoction of annatto in water is turbid, has a strong, peculiar odour and a disagreeable taste. Its colour is yellowish-red, turning orange-yellow with alkalis; at the same time the liquor clarifies and becomes more agreeable, while a small quantity of a whitish substance is separated from it which remains suspended in the liquid. If annatto be boiled along with an alkali, it dissolves much better than when alone, and the liquid has an orange hue.

With the liquor (1) Acids yield an orange-coloured precipitate, soluble in alkalis to a deep orange coloration. (2) Alum yields a deeper orange precipitate ; the liquid is of a pleasant lemon-yellow colour verging to green. (3) Sulphate of iron forms an orange-brown precipitate ; the liquor retains a very pale yellow colour. (4) Sulphate of copper gives a precipitate of a yellowish-brown colour, a little brighter than the preceding ; the liquor preserves a greenish-yellow colour. (5) Solution of tin produces a lemon yellow precipitate which falls slowly.

The colouring principle of annatto is soluble in oil as well as in alcohol. A solution in olive oil is used in France to impart a butter-yellow tint to margarine.

Turmeric.—The colouring principle of turmeric is furnished by the root (*rhizome*) of *Curcuma tinctoria* (Gub.), (*C. Longa*, Lin.), which flourishes in the East Indies. This substance is very rich in colour, yielding a brilliant orange-yellow, which is not, however, permanent. It is soluble in ether, alcohol, and coal-tar naphtha, and is an ingredient of delicate yellow lacquers. It is insoluble in water. It dissolves to a deep red colour in caustic alkaline solutions from which it is precipitated by acids. Turmeric powder is often adulterated, especially with pea-flour, which can easily be distinguished under the microscope. The Chinese is the best, especially Formosan, then that of Bengal, Pegu, and Madras. Bombay and Sind produce the worst. In buying the rhizome fingers, big, hard, heavy, and difficult to break are the best.

Saffron consists of the stigma of the flower of the cultivated saffron, *Crocus sativa*, indigenous to the East, but now cultivated generally throughout Europe. It requires a million flowers to make 2¼ lb. of saffron. It contains a yellow colouring principle, *safranine* or *crocine*,[1] which, when isolated, consists of a rose powder that dissolves with a yellow coloration in boiling water, alcohol, and alkalis. Saffron is often sold after being exhausted with alcohol and dried, but in that case instead of having a greasy lustre its surface is dull. It is often mixed with other flowers, with the fibres of dried beef, etc. These sophistications may be detected under the microscope. Certain formulæ for spirit varnishes still retain saffron, but it is principally used in cooking, confectionery, and medicine.

Indigo is a vegetable dye obtained by a process of steeping, fermentation, and oxidation from the leaves of *Indigofera tinctoria* and *I. cerulea*, natives of the East Indies and other parts of Asia. Indigo is met with in commerce in the form of small cubes or in flat, irregularly shaped pieces of a bright black or greenish-blue colour, and consisting of a dry paste containing among other matters a peculiar colouring principle, *indigotine*, which may be isolated by sublimation. It is insoluble.

Indigo is used in spirit varnishes, but only the very light kinds so as to avoid precipitation. When indigo is treated with sulphuric acid, and the product neutralized with soda, a blue colouring substance is obtained called indigo carmine, which finds a use in miniature painting. When indigo carmine is used to colour varnishes it is first ground upon a slab with a small quantity of the varnish and then incorporated with the bulk.

Alkanet Root.—The root of the Anchusia tinctoria cedes a red colour to alcohol, invaluable as a spirit varnish stain, as unlike aniline dyes it is free from fluorescence.

[1] Neither of these must be confounded with the aniline dyes of the same name.

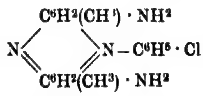
TABLE XCIV.—COAL TAR DYES USED IN SPIRIT VARNISH-MAKING.

Yellows.	Browns.	Reds.
Auramine, Con. O.	Cachou brown (D. G.).	Magenta.
Chrysoidine, A. C. Xls.	Dark brown (M. M. B.).	Janus red.
Vesuvin, Da O. 2R.	Janus brown (R. B.).	
Victoria yellow, Double Conc.		
Janus yellow (G. R.).		

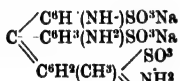
Violets.	Greens.	Blues.
Methyl violet.	Malachite green, Extra Xls.	Methylene blue.
	Brilliant " "	Janus blue (G. B. R.).
	Janus " (G. B.)	Fast blue (O.).

Blacks.
Coal black (O. I. II.).
Nigrosin (R. O. D.).
Janus black (O. I. II.).

Aniline Colours used in Lacquer Making, etc.—1. *Magenta* (Fuchsine), crystals a greenish metallic lustre by reflected light, but in thin sections by transmitted light their colour is red. It dissolves sparingly in water, imparting to it a crimson colour without fluorescence. Its aqueous solution is precipitated by tannic acid. It dissolves readily in alcohol, and in amylic alcohol (fusel oil, etc.). Only a small amount may be used to colour spirit varnish, otherwise it will dry with a bronze reflection which will mask the true colour.

Safranine 

2. *Safranine* is met with in commerce as a brown-red powder. It forms, when pure, red crystals with green reflection, which dissolve in water a red colour. It is precipitated by tannic acid from its aqueous solution. Its solution in alcohol is red with a fine orange fluorescence, and when mixed with auramine it colours spirit varnish a fine scarlet. It does not dissolve in ether. It is prepared by treating o-toluidine with nitrous acid and then oxidizing.

Acid Magenta 

3. *Acid Magenta.*—Commercial acid magenta is a green powder with metallic lustre which dissolves in water and alcohol with a bluish-red colour. Caustic soda discharges dilute acids, even CO_2 reproduce the colour. Its tinctorial power is only about one-half that of ordinary magenta.

Janus Red, m-Amidophenyltrimethylammonium + m-Toluidin diaz. + β-Naphthol,
$N(CH^3)^3Cl \cdot C^6H^4 \cdot N^2 \cdot C^6H^3(CH^3) \cdot N^2 \cdot C^{10}H^6 \cdot OH$.

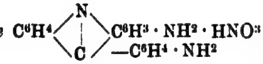
4. *Janus Red* is produced by diazotizing the base, coupling it with m-toluidine, diazotizing again and combining with β-naphthol.

5. *Picric Acid*, $C_6H_2(NO_2)_3OH$, although a coal-tar colour, was discovered so far back as 1799. It is met with in the form of pale

lemon or straw yellow foliæ, which melt at 122·5° C. It may be sublimed, but with the greatest of care, as it is highly explosive, and its alkaline compounds even more so. It may be used by itself to colour varnishes yellow or in combination with suitable blues for green lacquers, etc. It is produced by the action of nitric acid upon carbolic acid. It is also generated when silk, wool, leather, aniline, indigo, resins, etc., are acted upon by this acid. It only dissolves in 165 times its weight of water, but 1 part in 1000 communicates a distinct greenish-yellow colour and a most intense bitter taste to the water used for its solution; but it dissolves easily in alcohol, ether, and benzene.

The commercial article is liable to adulteration. It should be completely soluble in benzol, and in water acidified with sulphuric acid and in 10 parts of alcohol. Any matter insoluble in alcohol would indicate mineral matter, sulphate or nitrate of soda. The solution in ammonia should give no precipitate with calcium chloride (absence of oxalic acid). Sugar may be detected by neutralizing with soda and extracting with dilute alcohol. The sugar dissolves; the picrate of soda is insoluble.

6. *Victoria Orange*, $\overset{ONa}{\underset{(NO_2)_3}{C_6H_2CH_3}}$, is a variable mixture of the sodium salts of o- and p- dinitro cresol. With trinitro metacresol it forms a reddish-yellow powder which dyes wool a yellow-orange. It is poisonous, but none the less is used to dye liquors, etc. Victoria orange can be readily sublimed by placing the suspected sample between filter paper and heating to 100° C. If this dye be present the paper will be stained yellow. The ammonium salts of nitro cresols are used as explosives. Thus the ammonium salt of trinitro cresol is the chief constituent of the Austrian explosive ecrasite and probably also of the French cresylite. All these explosives, picric acid, and such like, should be stored outside the building. Picric acid accidents are somewhat numerous in colour factories, and no doubt are the cause of fires and explosions which cannot be traced to their source. Spirit varnishes stained with nitro compounds are highly dangerous and should be branded as such.

Phosphine 

7. *Phosphine* is an orange-yellow powder, soluble in water, from which it may be precipitated by tannic acid. Alkalis precipitate it in yellow flocks soluble in alcohol and ether. The precipitate is coloured brown-red if sample impure. If concentrated hydrochloric acid be added to a solution of phosphine, a precipitate of the di-acid salt is produced which is freely soluble in water. It is soluble in alcohol and also in ether, imparting to the solution a magnificent yellow colour with intense green fluorescence. Aqueous solutions of phosphine yield in the cold, with a 1 per cent solution of nitrate of

potash, an immediate characteristic red crystalline acicular precipitate of chrysaniline nitrate.

$$\textit{Auramine}\ HN = C{<}^{C^6H^4 \cdot N(CH^3)^2}_{C^6H^4 \cdot N(CH^3)^2 \cdot HCl}$$

$$\textit{Auramine G},\ HN = C{<}^{C^6H^3(CH^3)o \cdot NH \cdot CH^3}_{C^6H^3(CH^3)o \cdot NH \cdot CH^3 \cdot HCl}$$

8. *Auramine.*—Commercial auramine is a yellow powder which yields a yellow solution with water. Alkalis give a white milky percipitate soluble in ether without fluorescence. Mineral acids gradually decolorize it in the cold. Sodium amalgam gradually decolorizes the alcoholic solution, which, on the addition of water, yields a colourless precipitate, yielding a deep blue coloration with hot acetic acid. Zinc dust and acetic acid give a green colour. Auramine, Con. O. (M. L. and B.) is recommended for spirit varnishes.

$$\textit{Chrysoidine}\ C^6H^5 \cdot N^2 \cdot C^6H^3{<}^{NH^2}_{NH^2 \cdot HCl}$$

9. *Chrysoidine.*—Commercial chrysoidine consists of deep violet crystals with metallic lustre, dissolving easily in boiling water and in alcohol. Dyes wool orange-yellow. The aqueous solution coagulates into a deep blood-red gelatinous mass. Sulphuric acid gives a yellowish-brown coloration. Tin crystals decolorize. Basic acetate of lead gives an orange precipitate. Mixed with methyl green gives a fine olive-green. Chrysoidine A. C. Xls. (M. L. and B.) is recommended for spirit varnishes.

$$\textit{Bismarck Brown}\ C^6H^4{<}^{N^2 \cdot C^6H^3(NH^2)^2}_{N^2 \cdot C^6H^3(NH^2)^2}$$

10. *Bismarck Brown.*—Commercial Bismarck brown is a blackish-looking powder, dissolving in alcohol and water with a red-brown colour. Dyes wool orange-brown; sulphuric acid turns the aqueous solution yellowish-brown. Tin crystals and hydrochloric acid discharge the colour. Basic acetate of lead gives a brown precipitate. The aqueous solution does not gelatinize on cooling (*distinction from chrysoidine*). This colour is greatly used by French polishers as a mahogany stain.

11. *Cachou Brown*, M. L. Br.

Diaminbrown M.

Benzidin$<$ Salicylate / β-Amidonaphtholsulphonate γ (alkal. comb.).

Diaminbrown V.

Benzidin$<$ β-Amidonaphtholsulphonate γ (alkal. comb.). / m-Phenylendiamin.

$$OH \cdot C{\overset{\diagup C^6H^4 \cdot SO^3Na}{=}}\left[C^6H^4 \cdot N{<}^{C^2H^5}_{CH^2 \cdot C^6H^4 \cdot SO^3Na}\right]^2$$

$$\textit{Alkali Blue}\ C \begin{cases} C^6H^3 \cdot CH^3 \cdot NH \cdot C^6H^5 \\ C^6H^4 \cdot NH \cdot C^6H^5 \\ C^6H^4 \cdot NH \cdot C^6H^5 \cdot Cl \end{cases}$$

12. *Alkali Blue.*—Commercial alkali blue is met with as a brown powder or in lumps, which dissolve in 5 parts of water and in

alcohol. Acetic acid colours blue and deposits a blue precipitate on boiling. Hydrochloric acid precipitates the colour with decolorization of the solution of the chemically pure colour. If carbonic acid is given off on acidification, soda is present; ammonia in excess decolorizes the solution; caustic soda gives a violet-red coloration, which turns to reddish-brown on boiling.

13. *Spirit Blue*, or aniline blue, is insoluble in water, but soluble in alcohol and ether. It is principally used in the manufacture of alkali blue. Its shade varies from blue to violet.

Janus blue, Indoin blue R. Safranin diaz. + β-Naphthol.

14. *Janus Blue.*—The hydrochlorides of safranine azo β-naphthol. The safranine azo β-naphthol is first prepared and the azoic so obtained treated by hydrochloric acid.

$$\textit{Methylene blue}\ N\begin{cases} C^6H^3 - N(CH^3)^2 \\ \quad > S \\ C^6H^3 = N(CH^3)^2 \cdot Cl \end{cases}$$

15. *Methylene Blue.*—The hydrochloride or the zinc chloride double salt (chlorozincate) is specially suitable for sky-blue tints.

16. *Fast Blue.*—R. B. spirit soluble. An induline produced by heating amidoazo-benzol (nitrophenol) with aniline and aniline hydrochloride.

17. *Light Green S. F. Yellow Shade.*—This dye comes into commerce as a brown amber-looking powder, which dissolves in water and alcohol. The aqueous solution is completely precipitated by basic acetate of lead yielding a magnificent green lake. It is a truer green and much more permanent to light than any other aniline green, and can be safely recommended to the varnish-maker.

$$\textit{Malachite green},\ C^6H^5 \cdot C\begin{cases} C^6H^4 \cdot N(CH^3)^2 \\ C^6H^4 \cdot N(CH^3)^2 \cdot Cl \end{cases}$$

Tetramethyldiamidotriphenylcarbinol-chloro-zincate,-picrate, or -oxalate.

18. *Malachite Green* is prepared by condensing dimethyl aniline with benzoic aldehyde in presence of a dehydrating agent, zinc chloride or anhydrous oxalic acid, is met with in crystalline plates of a green metallic lustre, which dissolves freely in water, alcohol, and amylic alcohol (distinction from methyl green). Hydrochloric acid gives an orange coloration, the green colour being restored by dilution; tin crystals a green precipitate. Bleaching powder, ammonia, and alkalis decolorize, very fugitive. When heated to 100° C. it does not turn violet (distinction from methyl green).

Brilliant green, Tetraethyldiamidotriphenylcarbinol.

19. *Brilliant Green* is the tetraethyl derivative corresponding to malachite green. It thus only differs from malachite green by containing the radical ethyl instead of methyl. In commerce it occurs as the zinc chloride double salt or sulphate. Brilliant green extra crystals (M. L. and B.) are recommended for varnish-makers.

20. *Janus Green* (M. L. Br.) is obtained by the action of dimethylaniline on diazo safranine.

Methyl violet B, 2 *B*, Pentamethyl-pararosanilin hydrochloride.

$$C\begin{cases} C^6H^4 \cdot NH \cdot CH^3 \\ C^6H^4 \cdot N(CH^3)^2 \\ C^6H^4 \cdot N(CH^3)^2 \cdot Cl \end{cases}$$

21. *Methyl Violet* is a mixture of tetra-, penta-, and hexa-methylated rosinates. It is produced during the oxidation of dimethyl aniline by means of salt, copper salts, and phenol.

PART IV.

METHODS OF MANUFACTURE.

CHAPTER XXI.

PRINCIPLES AND PRACTICE OF SPIRIT VARNISH MANUFACTURE.

Definition.—Spirit varnishes are more or less thin, more or less viscous, colourless or more or less coloured, more or less opaque or transparent solutions of one or more natural resins, e.g. shellac or sandarach, etc., in one or more appropriate volatile solvents which leave on evaporation a thin, more or less resistent film which both adorns and protects the object on which it is applied.

Or spirit varnishes may consist of more or less viscous solutions with similar properties of a natural or artificial asphaltum in turps or of an artificially produced solid such as nitro cellulose, in an appropriate volatile solvent such as amyl acetate. Or again, the solid constituent of spirit varnish may consist of an artificially produced resin generated by the action of say formaldehyde on various organic bodies. Or these various classes of solids, natural resins, artificial resins, natural bitumens, and artificial pitches and other artificially produced solids may each and all enter into the composition of a spirit varnish, and the solvent instead of being a simple body like ethyl alcohol may consist of a mixture of ethyl, methyl, and amyl alcohols, ethyl and amyl acetates, ether, acetic ether, benzene or its chlorides, or other derivatives, together with the chlorides of the other hydrocarbides, homologous with benzene occurring in coal-tar. When it is added that a spirit varnish may be coloured by any natural dye soluble in alcohol or any coal-tar dye soluble in the same solvent, it will be seen that if spirit varnishes are usually fairly simple solutions of one or two resins in methylated spirits or in spirits of turpentine, yet on the other hand spirit varnishes may be of a highly complex nature indeed. On evaporation of the liquid solvent or solvents with or without the aid of artificial heat, the more or less unchanged resins or solids are left in the form of a thin layer of dried varnish, which varies on the one hand with the nature and relative proportion of the resins and solids to each other, and the ratio of solvents to substances dissolved on the other hand. The resin or solid is supposed to be recovered unchanged on the evaporation of the solvent as a layer of varnish, and this coat to exhibit all the merits and defects of its constituent solids, but this is only true

in a very general sense. There are no data as to how far such resins may undergo chemical change during solution or become oxidized in contact with the air both during and after the evaporation of the solvent, nor whether the solvent has got any chemical affinity for the resin, nor the one resin for the other, nor whether such affinity comes into play during the making, applying, and spontaneous evaporation of a spirit varnish. Hard resins yield bright spirit varnishes, but such varnishes leave brittle films. Varnishes from soft resins are less lustrous, but their elasticity diminishes as their essential oil disappears. By dissolving several resins together, their bad qualities may be so neutralized as to yield a varnish fit for the end in view, an end unattainable by the solution of any one single resin. By judicious admixture of cheap resins, a varnish approaching that got from a more costly resin may be prepared. But it is necessary at the outset to know the kind of varnish which each resin yields, in what points it excels, and in what points it is deficient, and here comes in the important point of the comparative hardness of resins. *Scale of Hardness.*—(1) Amber, (2) Copal, (3) Dammar, (4) Shellac, (5) Mastic, (6) Sandarach, (7) Rosin, (8) Elemi, (9) Turpentine, (10) Burgundy pitch, (11) Asphaltum. The hardness of the various resins classed as copal is given on pp. 9 and 43, Vol. II. Hard resins, like amber and copal, yield on evaporation of the solvent non-tacky, hard, lustrous, but rather brittle coats. These resins excel as oil varnishes, so much so that the amber oil varnishes used in colour-printing on tinned iron leave a film on the sheets of such elasticity that when the tinned sheets after printing have had to be milled and the printing perforce elongated, the continuity of the varnish is perfect, such is its enormous elasticity. But this elasticity is greatly due to the oil and not altogether to the pyrosuccin. The only oils soluble in spirit and thus available for spirit varnish manufacture is castor oil, but it does not dry well and its addition to spirit varnishes unless unavoidable is to be deprecated. Sandarach and mastic yield fairly hard but much more brittle films, which, moreover, are somewhat tacky till thoroughly dry. Elemi, Venice turpentine, Burgundy pitch, gum, thus yield elastic, but very tacky coats; their elastic-imparting capacity depends on the essential oil which they contain and retain but only for a time. Such elasticity is thus evanescent. Shellac is the spirit varnish resin *par excellence*. It may be termed the *ne plus ultra* of spirit varnish materials in so far as it is unexcelled in yielding a varnish which produces a tougher and more elastic coat than that got by the use of any other natural resin. Not only so, but for ease of application, as in French polishing, shellac varnishes occupy a perfectly unique position. The same amount of elasticity as is obtained in the film left by a shellac spirit can be got from no other resin unless it be incorporated in an oil varnish, then the elasticity of the varnish is due to the oil. It is a pity that varnishes supposed to consist wholly and solely of shellac should be adulterated with Manila copal and

rosin. Exceptions were taken in certain quarters to this statement in the first English edition of this treatise. It is to be hoped that those who then did not know better have by now become more enlightened.

Rules Regulating Solution of Resins in Mixed Solvent (Tixier).—Take C soluble in a fluid S but insoluble in another I. If a known weight x of C be dissolved in a known weight y of S, a certain weight of I can be added to the solution without producing any turbidity. Let the greatest amount of I that can be so added $= Z$. Then z, though depending on the nature of S and upon the concentration of the solution as well as upon the nature of C and upon the temperature, is independent of x within very wide limits. The equation connecting these quantities has been found to be

$$\frac{y}{Y + Z} = k \text{ a constant.}$$

Tixier claims from above data to be able to classify varnishes into perfect varnishes, consisting of simple solutions of C in S, and imperfect varnishes, consisting of the same solutions with more or less I in them. Each of these he subdivides into two sub-classes. Sub-class A quick-drying, sub-class B slow-drying, and these sub-classes may be still further differentiated thus :—

Varnishes	perfect	quick-drying	tacky
		slow-drying	non-tacky
	imperfect	quick-drying	tacky
		slow-drying	non-tacky

The quality of a varnish, as we have already seen, depends principally on the resins employed and the stability of the solution. The kind of resin or resins, and the proportions thereof, also vary with the kind of varnish it is desired to make and the purpose for which it is to be used.

More or less volatile liquids are used as solvents—such as methylated spirit, spirits of turpentine, ether, etc. The harder the resin and the more volatile the solvent, the quicker does the varnish dry; but the coating does not wear so well, being easily affected by alterations of temperature. If the varnish be too thin the coat will "pit"—i.e. become dotted with numerous small holes; on the other hand, if too thick, the resin, being very brittle, will shell off very easily. The quantity of solvent, or solvents, required for any particular spirit varnish will depend not only on the thickness, etc., of the coating desired, but also on the nature of the resin, or resins, and their degree of solubility in the solvent, or mixture of solvents, as well as on the greater or less rapidity with which the solvent, or the different volatile ingredients of the mixture of solvents, volatilize. Speaking generally, *the consistency of a varnish should harmonize with that of the solvent. The more volatile the solvent the thinner should be the varnish, the necessary thickness being imparted by applying several thin coats.*

Thinning Down Concentrated Varnishes.—Some manufacturers prepare a thick varnish, which they thin down to the requisite consistency as they send it out, according to the nature of the "orders" they are making up. In actual practice, 2½ parts of solvent are used for every part of resin; but when the varnish has afterwards to be bleached or filtered, etc., a larger proportion of solvent may be used, and the excess afterwards recovered by distillation.

Mixing Separate Standardized Solutions of Individual Resins to Produce a desired Varnish.—When the manufacturer has a large trade in a variety of varnishes of very different compositions, in each of which several resins are associated together, no good purpose is served in multiplying operations by preparing each of those varnishes singly. It is far better and more economical to make separate solutions of each of the resins and mix them, when required, in the desired proportions, according to the particular varnish it is desired to send out. In order to save calculations, and thus be in a position to make the necessary mixings expeditiously, all the resin solutions should if possible be of the same strength, i.e. the ratio of resin to solvent the same in each case (see Reh's method, pp. 382, 407).

Thinning Down Concentrated Varnishes.—Working in the above manner, the solutions of each of the resins must be at least as thick as that used in actual practice; it is possible to thin down a varnish with spirits of turpentine or methylated spirit, but it would be a costly job to concentrate it. Some varnish-makers therefore prepare several thick solutions which they thin down, and blend, the one with the other, when making up their varnish orders. Reference to the table given on p. 436 will show, as regards methylated spirit, solutions of rosin, the thickness and viscosity at different strengths, and each varnish manufacturer could at no great trouble and with great profit to himself construct a similar table for each varnish resin and each solvent. On the Continent, where they use much thinner spirit varnishes than we do here, about 2½ lb. of solvent are used for every lb. of resin, i.e. about 2 to 3 lb. to the gallon, but when the varnish has afterwards to be bleached or filtered they are said to use thinner solutions still, and recover the excess of solvent by distillation. However that may be abroad, the British excise laws do not sanction any such method of working. Moreover, in Britain 5, 6, and 7 lb. of resin to the gallon of methylated spirit are not uncommon, and spirit varnishes are not often filtered and still less seldom bleached. The principal solvents used in spirit varnish manufacture are methylated spirits and spirits of turpentine. *Alcoholic Strength.*—When alcohol is the solvent or vehicle used, the quicker the varnish is required to dry the stronger must be the alcohol. In all cases it should contain 90 per cent of anhydrous or absolute alcohol, but abroad they consider when it is required to thin the varnish 83 or even 80 per cent, alcohol answers very well. But it is better to try on a small quantity how far the alcohol can be reduced before starting to thin down the bulk of the varnish, for

if too weak alcohol be used the water which it contains will throw the resin out of solution, rendering the varnish turbid, and give more trouble and annoyance in again clarifying it than would compensate for any profit incidental to the process. It is also necessary to note whether the varnish becomes cloudy on lowering the temperature. Moreover, too dilute alcohol imparts a tendency to "bloom," etc., to the resultant varnish.

Spirits of turpentine always leaves a residue on evaporation. It partially resinifies owing to the absorption of oxygen, and this resin or balsam is embodied in the resultant coat, which consequently does not dry so quickly as a methylated spirit varnish or one made from rectified shale naphtha, petroleum naphtha, or coal-tar, etc., naphthas. But spirits of turpentine does not evaporate so quickly as methylated spirit; the coating is thus formed more slowly, and therefore in a more uniform and free manner, thus diminishing pitting and cracking. Recently distilled spirits of turpentine does not oxidize or resinify to any great extent, but when it has been stored for some time with free excess of air it oxidizes very appreciably, and the thick gluey balsam left on evaporation seriously injures the quality of the varnish. Ordinary crude or deficiently rectified Russian spirits of turpentine leave a bulky residue on evaporation and cede much tarry matter to caustic soda. The use of spirits of turpentine as a solvent for varnishes for indoor work is restricted by its injurious action on the nervous system of the painters and decorators who inhale its vapours in too great a quantity. But the diminished amount of oxygen in the superincumbent atmosphere due to its rapid absorption by the spirits of turpentine and resin must of necessity exert an injurious effect. In what state the volatilized spirits of turpentine diffuses through the air is another point which claims attention. It is more than likely that it is diffused as a substance allied to camphor. We know that it resinifies slowly when in the liquid form it comes in contact with air. But how much quicker must be its oxidation in the gaseous form when diffused through the air even of a comparatively confined space. Looking at the matter from this point of view, it is not difficult to account for the condensable gaseous emanations from "white-lead" paint. They no more emanate from white lead than they do from the China clay with which it is sophisticated.

Influence of Resinification Products of Turps on the Drying of Varnishes, etc.—Reh's assertion that small portions of soft resin or the resinification products of oil of turpentine will retard the drying of varnishes, induced Ragg to investigate the question more thoroughly. He found that the resinification process is effected in two stages, the first being characterized by the formation of a thick brown oil, which is transformed, during the second stage, into a resin with the consistence of galipot. Each of these products was added to copal varnish, in quantities varying from 44 to 135 per cent of the amount of copal present. The results showed that

neither of them adversely affects the drying properties of the varnish, even when the quantity added far exceeds that present in practice, though an injurious effect may be produced in the case of linseed oil varnish or with oil paints that do not contain saponifiable oxides of the heavy metals.

Nowadays the varnish-maker has at his disposal much cheaper solvents, such as benzol, solvent naphtha, etc. It is cheaper in some cases, and, where practicable, to make an original thick solution of resin in these solvents and then thin down with methylated spirits or spirits of turpentine, gasoline, petroleum ether, etc. A saving of time is thus effected, as very often the resins dissolve more freely in these solvents than in either spirits of turpentine or alcohol.

It has also been found advantageous in France to replace spirits of wine by wood spirit on account of the difference in price, or by amylic alcohol (rectified fusel oil), which volatilizes less rapidly, but few workmen who once used an amylic alcohol varnish would care to do so a second time. The amylic acetate, however, so much used as a solvent for celluloid varnishes is more pleasant. In some cases a complex mixture of the most varied solvents is used, of which the following, recommended for dissolving copal, is typical, viz. equal parts by volume of carbon disulphide, spirits of turpentine, benzene, wood spirit. But a mixture of liquids with a wide range of boiling-points is to be avoided, unless closely allied, e.g. gasolene and petroleum naphtha. Otherwise mixtures of solvents of different boiling-points give rise to irregular, uneven evaporation with all its attendant evils. In fact, even if only single solvents be used to dissolve the resin the nature of that single solvent appreciably modifies the resultant varnish. A very volatile solvent makes the varnish have a tendency to pit or pinhole, whilst a solvent which evaporates slowly may need heat to volatilize it more rapidly or to expel the last traces; but then the coating may be liable to scale off. Varnishes containing shellac are turbid owing to the presence of a wax natural to the resin insoluble in alcohol. But as this insoluble wax rather improves the varnish than otherwise, no attempt is made to remove it.

Dissolving the Resins: *Cold Process.*—This simple operation is not always carried out very rationally. The continental authors dwell very much on the fastidious care with which the resins should be selected. They go upon the principle that if different samples of the same resin do not always dissolve equally readily in the same solvent, yet pieces of the same degree of hardness, colour, and brilliancy all dissolve with the same rapidity and to the same extent. It is thus advisable, they say, to sort out the pieces as received from the gum merchants according to colour, transparency, etc., so that solution may go on more regularly and more homogeneous varnish be obtained; but this sorting or garbling is left in Britain to the gum cleaners, who mostly restrict themselves to simply washing and cleaning the gum. A spirit varnish-maker has no time for such

fastidious minute details. He buys what suits his purpose. He buys on occasion copal dust, dammar dust, kauri dust, and works them up such as they are to the best advantage. If a parcel of resin did not suit him, in the language of the trade, "he would not even look at it". Copal is not assorted, the dust rejected as unsuitable for oil varnishes is used. The resins are reduced to the size of a lentil or finer, for the finer the powder the easier does the resin dissolve; but if the solvent be given too much resin to run all at once, the particles will agglutinate together and take longer to dissolve. Further, by the solution of the resin in the solvent there is formed a liquid of greater density than the original solvent. This is especially the

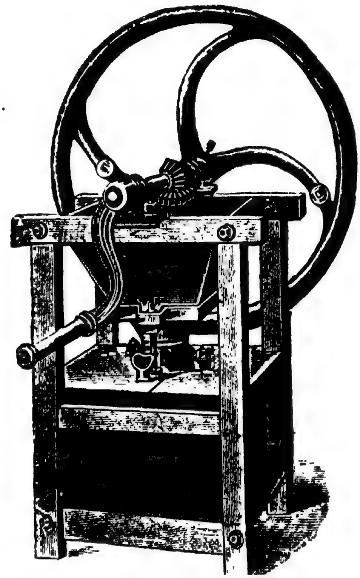


FIG. 42.—Hand-mill for Spirit Varnish Resins.

case with the bottom liquid in contact with or in proximity to the resin. This liquid ought, therefore, to be renewed by agitation, so as to bring fresh portions of the solvent in contact with the resin and keep the solution always of the same density throughout the entire mass. This prevents the powder from agglutinating and prevents solution from only going on at the bottom of the vat. The whole mass of effective solvent is thus able to exert its solvent action on the resin instead of the saturated ineffective portion at the bottom of the vat.

When working with small quantities the necessary agitation can be produced by manual labour, viz. by using a barrel as the dissolving vessel—driving the bung in tightly and rolling it about

the floor until complete solution is effected; or if cramped for space a clean empty barrel may be stood on end, the other end knocked out, the resin and solvent added, and the whole stirred from time to time with a large wooden spatula. On the other hand, when work-

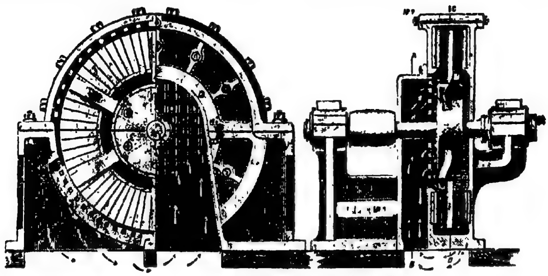


FIG. 43.—Disintegrator for crushing Resins.

ing with larger quantities, it is better to use a mechanical agitator; but with open vessels a loss of solvent by evaporation will be unavoidable. It is therefore preferable to use closed mixers in which the resin and solvent are continually stirred.

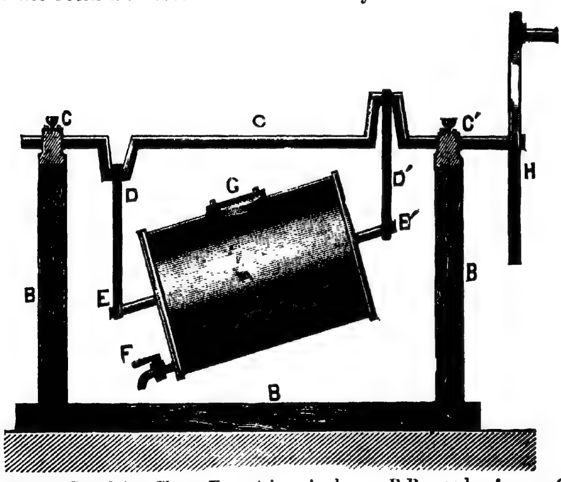


FIG. 44.—Revolving Churn Excentric. A, churn; B B, wooden frame; C C C', horizontal shaft; E E', inclined shaft; F, tap for running off varnish; G, charging manhole; H, driving wheel.

A truncated tub-shaped wooden vessel fitted with a mechanical agitator forms a simple mixer. But it has a great drawback, it being customary to leave the substance to dissolve of its own accord in contact with the solvent for several hours, so as to obtain more rapid solution when the agitator is put in motion. Now, in working

with some resins—shellac in particular—a thick, stiff, swollen mass is obtained, consisting of the undissolved gum embedded in a viscous saturated solution of the solvent, which, on starting the agitator, either breaks the blades or the shaft which carries them.

In preference, either a cask laid horizontally (Fig. 47), supported by and turning on two pivots placed in the axis of length, or a cylindrical receiver, supported by and turning on two opposite pivots on its cross axis, is used. The opening by which the materials are introduced is closed by a lid, which presses against an india-rubber

Fig. 45.—Electrically welded steel Varnish Churn.

washer; a wooden cross-piece, through which two bolts pass, is screwed up by the nuts so as to press strongly against the washer, and thus hermetically seal the apparatus. This arrangement is much better than the old method of closing by means of a screw stopper, as we thus avoid the encrustation in the thread of the screw, and on emptying the apparatus the mouth can easily be freed from any varnish which would solidify there. A revolving drum-shaped churn A (Fig. 44) may also be used, the two pivots EE of which, placed in the axis of length, are connected by two vertical rods DD^1 with a horizontal shaft bent disymmetrically at the points of attach-

ment. As the shaft revolves each end of the cylinder occupies alternately the higher and then the lower position, and thus a more complete commingling of the contents of the churn from top to bottom and from end to end or side to side as it were is effected. It takes six to seven hours to make 40 gallons of spirit varnish whether agitated by hand or by a crank or by a mechanical agitator.

The principle upon which steel barrels and drums are constructed has been applied to the production of a churning machine for making spirit varnish. It appears that the bilge in the body of barrels is of practical utility when it appears in a varnish churn. The accompanying illustration needs but a few words of explanation to make the operation of the machine intelligible. Those who are familiar with electrically welded steel barrels and drums will quickly see the advantages of this mixing machine.

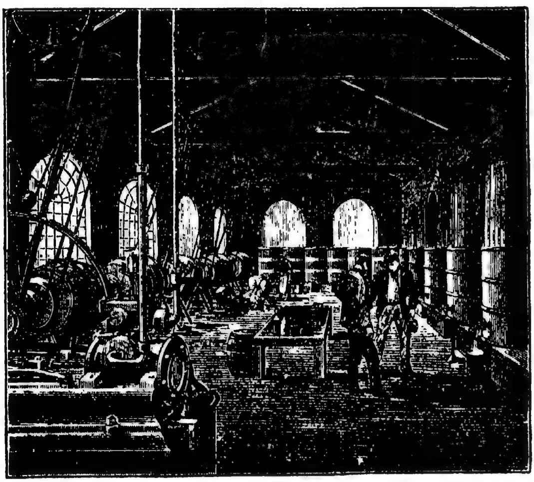


FIG. 46.—Spirit Varnish-making in an English spirit varnish factory.

The cask (Fig. 45) is curved (or "bilged") inside and outside like a wooden barrel. This is found most convenient for emptying, since all the material to be emptied gathers by gravity to the centre of the curved body. The curved form is found advantageous in the mixing, because, as the cask rotates, an eddy is formed in the centre of the barrel, which mixes the contents more effectually than would be the case if the barrel were cylindrical. Wooden varnish-mixers are often cylindrical on the inside, though curved on the outside. Additional strength is gained by the axle being carried right through the cask. The smoothness of the cask inside prevents the varnish accumulating in lumps, if the cask should be temporarily out of work. Another important feature is that all the joints, including those of the axle at its passage through the ends of the cask, are

electrically welded, so that all leakage is prevented. Naturally, a steel cask resists wear and tear more effectually than a wooden barrel. The churns may be driven by a steam engine, a gas engine, or an oil engine, or by an engine fed by a suction-gas plant.

The output of varnish may be increased by applying heat to the steel cask, which can be done safely without injury to the cask; indeed, the casks are sometimes run in hot water for this very

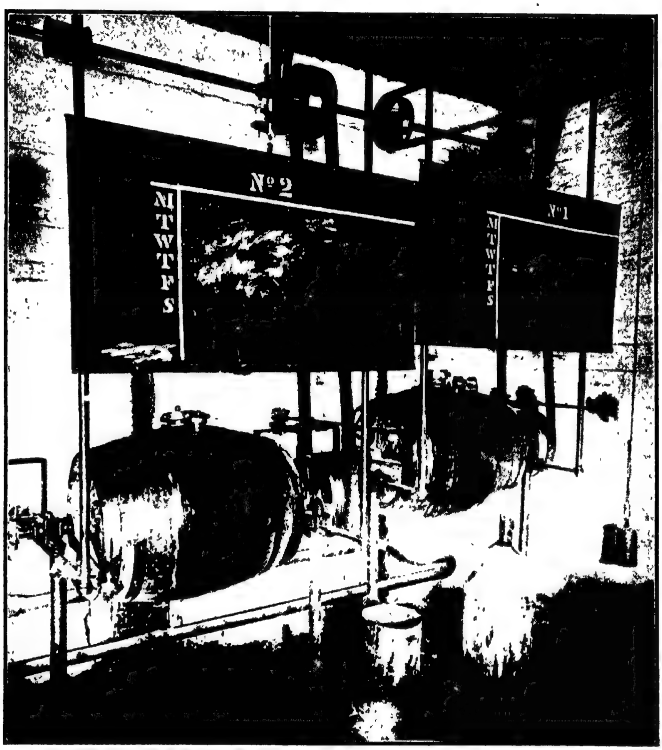


FIG. 47.—Spirit Varnish-making.
[Photo by Mr. C. Harrison, Borough Polytechnic.]

purpose. This increases the output of varnish in cold weather. These machines are made in all sizes, the smaller ones being of a simpler type than the one shown in the illustration. The machine shown has a capacity of about 530 gallons. The cask is 6 feet in diameter at the centre. The rack arrangement attached to it is intended to keep the cask in any desired position for filling or emptying; it also adjusts the cask when rotation ceases.

Whatever precautions be taken in spirit varnish-making the varnish is always turbid, and must therefore be clarified. This is effected by allowing the varnish to rest quietly in large bottles or metallic reservoirs in a fairly warm place where there is no vibration. The clear liquid is decanted.

Filtration.—But when very pale brilliant varnishes as clear as crystal are required they must be filtered at the outset by passing them through a linen filter placed in a wooden funnel fixed above the reservoir. When time is an object, filtration is hastened by using

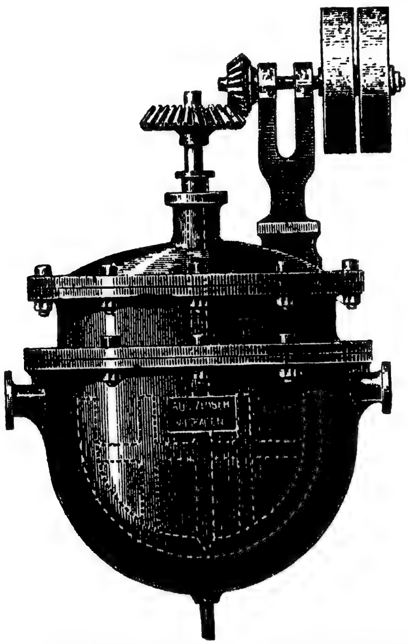


Fig. 48.—Steam-jacketed Fusion and Solution Vessel fitted with agitator driven by cogwheel gearing.

narrow linen bags as filters. These bags measure about 12 inches broad by 30 inches deep and are enclosed in another envelope of coarse sacking 8 inches wide by 30 inches deep; working thus the interior bag cannot swell completely with the pressure of the liquid, and folds are thereby formed which facilitate filtration in the beginning. Further, a greater number of these filters can be suspended at the exit of a special form of funnel.

The operation is followed by the indications of a glass gauge on the side of the reservoir. The temperature of filtration should be kept at about 20° C. (68° F.).

Loss of solvent occurs in filling the funnel, which loss is accentuated by its being closed by a loosely fitting lid. Consequently the liquid filling the funnel thickens, filtration becomes slow, and the

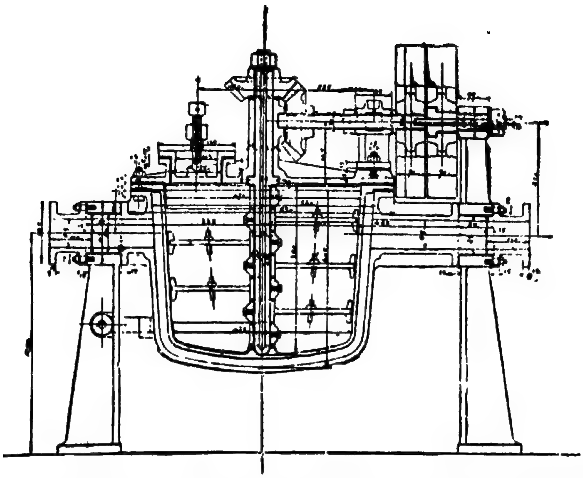


Fig. 49.—Drawings to scale of Steam-jacketed Fusion and Solution Vessel, showing agitator for use in spirit varnish-making.

quantity of thick solution retained by the impurities causes considerable loss.

Any loss due to imperfect closing may be done away with by

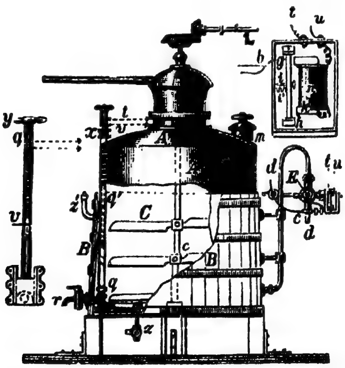


Fig. 50.—Steam-jacketed Solution and Fusion Vessel fitted with agitator and cog-wheel gearing with automatic electrical regulators.

using the following arrangement. The funnel (Fig. 52, T) is closed by a tight-fitting lid D, which is connected with the lid of the receiver F by an india-rubber tube K. The air displaced by the

filtered varnish passes from the receiver F through the india-rubber tube K into the funnel T, and thus occupies the space vacated by the varnish by which it was displaced. Filtration can thus go on notwithstanding the fact that the apparatus is hermetically sealed. This arrangement is very suitable when working on the small scale, and with small apparatus where the funnel fits tightly into the receiver.

Philippe's Varnish Filter.—Fig. 51 consists of a wrought-iron cylinder fixed on a tripod or any other convenient support. The cylinder is closed at both ends by two lids fixed by bolts and nuts. The lower lid is perforated. In the upper lid is an entrance for the varnish to be filtered. This entrance may be fitted with a funnel and a tap as shown in Fig. 52. Another pipe is fitted up as a pressure pipe for compressed air, carbonic acid steam. A pressure gauge is fixed to the filter to control the pressure. The filtering medium consists of a more or less fine and tightly woven cloth of cotton fabric, copper, iron, or felt. This cloth is supported by the perforated bottom, and a joint is got by a special rubber washing forming between the cylinder and the lower lid of the filter. The varnish being run into the filter, the capacity of which is variable, compressed air, gas, or steam, as the case may be, is turned on. This pressure forces the varnish to flow through the filter cloth. The filtered varnish is collected underneath the filter, and the latter can be specially fitted up for the purpose. The choice of filtering medium varies with the nature and consistence of the varnish to be filtered.

Simultaneous Solution and Filtration.—It has been attempted to dispense with agitation in making varnish by adopting an arrangement which both dissolves the resin and simultaneously filters the resultant varnish. Agitation prevents the finely powdered resin from agglutinating at the bottom of the vessel and replaces the resin-saturated liquid in contact with the resin by fresh quantities of the solvent; or rather it prevents this saturated solution from forming by continually renewing the solvent in contact with the resin. A somewhat similar occurrence takes place when we add sugar to tea to sweeten it. If we do not stir the tea until we have emptied the cup to the bottom we might almost as well not sweeten it at all, for the great bulk of the sugar remains either undissolved or in the form of a saturated solution which prevents further solution taking place without agitation to diffuse the saturated solution uniformly through the whole volume of the liquid. Agglutination may, however, be prevented by isolating the particles of resin from contact with each other by interposition with an inert body, thus accomplishing one of the objects of agitation. The second object of agitation can also be effected by an arrangement based on the fact that the saturated solution at the bottom is denser than that at the top. By suspending the substance to be dissolved as near the surface of the solvent as may be, the solution formed by the contact of the resin and the solvent, on account of its greater density, sinks to the bottom

as soon as formed, whilst its place is taken by a less saturated portion of the solvent, which in turn falls to the bottom ; in fact, by

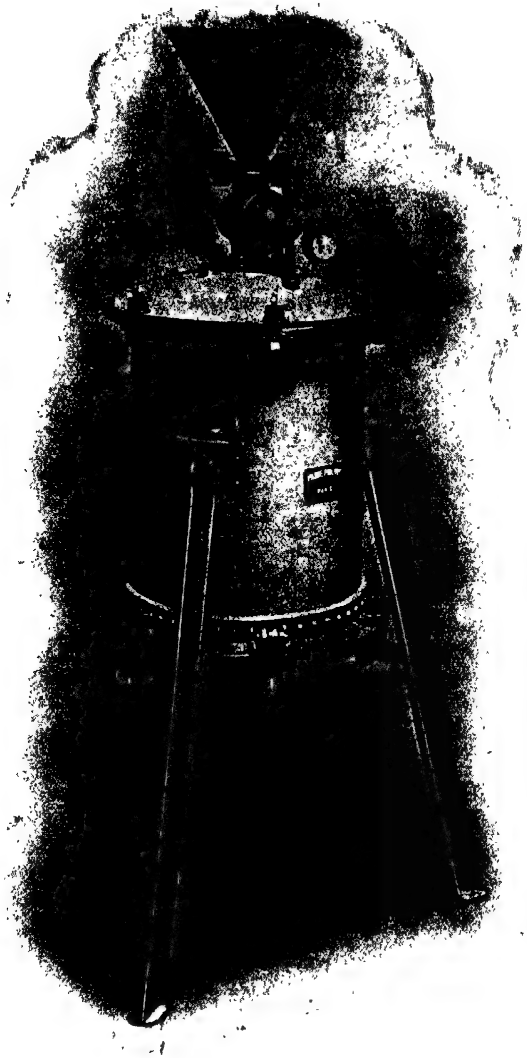


FIG. 51.—Philippe's Varnish Filter.

taking advantage of the diffusion of liquids we are able to dispense with agitation altogether, and as the mixture of resin and inert sub-

stance has to be suspended in a bag near the surface of the liquid, filtration is effected at the same time. Equal parts of resin and inert substance are used; the latter may be either fine washed and united silver sand or ground glass freed from too fine particles by sifting. This mixture is first placed in a double envelope of filter paper and then tightly packed in coarse muslin, and the whole finally placed in a linen bag which dips into the solvent. Working in this manner, all impurities and insoluble matter are retained in the bag; moreover, the liquid retained by the impurities and the linen not being thickened by evaporation, the loss is thus diminished. On the large scale linen or muslin-lined wire baskets of a size and shape to suit the reservoir are used. Several folds of filter paper are placed

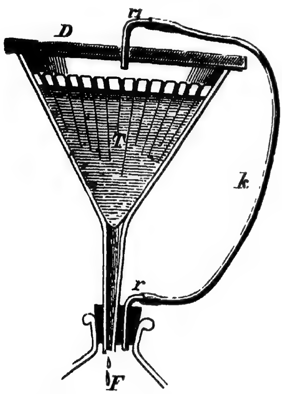


FIG. 52.—Varnish filtering arrangement. *F*, glass receiver closed by two-holed cork; *k*, rubber; *r*, *r'*, glass tubing connecting *T* with *F*; *D*, wooden cover with india-rubber ring fitting tight on to ground rim of funnel.

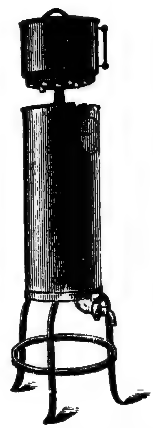


FIG. 52A.—Bag Filter.

on the top of the muslin. The mixture of resin and inert substance is then placed in the basket and covered with filter paper and linen. The baskets are best made of galvanized iron wire. Copper wire should be rigidly excluded. The spirit varnishes prepared by the methods described are erroneously termed colourless varnishes, although they have often a very pronounced colour. Even when the palest resins are used they are of a more or less deep yellow tint. This tint may be removed by special treatment. Animal charcoal or bone-black in the form of coarse sand is the most energetic decolorizer. The phosphate is removed from the bone-black by treatment with acid, preferably hydrochloric acid, and after well washing and drying the residual carbon is fit for use. Rather coarse charcoal should be used, because although finer charcoal has a more powerful bleaching action, yet the pores of the filter are soon choked up and filtration almost ceases, thus causing an unnecessary

loss of solvent. The best arrangement consists in running the varnish to be decolorized into a reservoir A with a side hole B near the bottom closed by a cork through which a tube D with tap C passes which leads the varnish into a receptacle G containing the animal charcoal. The extreme point of this receptacle passes through the tight-fitting lid H of the funnel J fitted into the cork of the neck of the vessel destined to receive the filtered varnish; a lateral tube L carries the air displaced in the receiving vessel up into the space

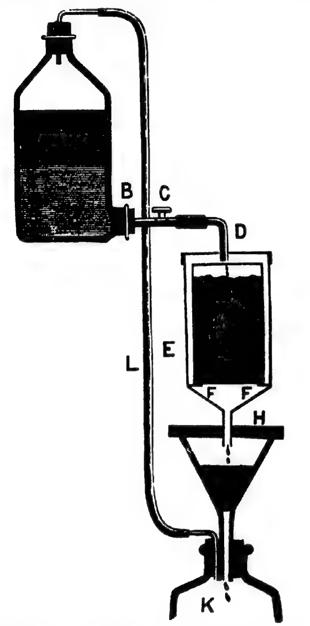


FIG. 53.—Apparatus for treatment of varnish by animal charcoal followed by filtration. A, vessel containing varnish to be filtered communicating from the top with receiver K, and through the bottom aperture B; tap C, bent pipe D, with funnel E, containing recipient G, charged with animal charcoal and resting on supports F, F, and through tube H, with filtration funnel J.

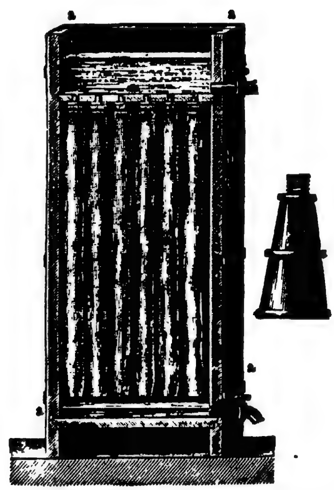


FIG. 53A.—Internal construction of Bag Filter. For varnish purposes they are usually of style as Fig. 52A.

vacated by the filtered varnish in the reservoir containing the varnish to be decolorized. There is thus no loss of solvent during filtration.

Coloured Spirit Varnishes; Spirit Varnish Stains.—In the manufacture of coloured varnishes the colouring matter is added to the finished varnish. If the colouring principle be soluble it is added in the state of solution, preferably in the same solvent as is used for the resin. These coloured varnishes are sometimes called transparent varnishes owing to the surface of the object remaining visible after

application. They are used to colour glass and are sometimes used for applying to fanlights. They ought to be very fluid, rich in colour, and dry rapidly to an elastic lustrous coating. The more common of these varnishes are generally made by dissolving shellac or sandarach, or a mixture of the two, in methylated spirit for dark, and bleached shellac for pale colours. They are generally made of greater body than usual, because the colouring solution thins them down slightly unless an aniline dye be used, when only a very insignificant quantity imparts the desired tint. A much superior or more refined and more delicately tinted varnish, a higher class article in every way, is got by tinting a celluloid varnish to the desired shade.

Spirit Varnish Enamels.—If an earth or mineral colour insoluble in the usual solvent used for the resin be used to colour the varnish the two are intimately mixed in a revolving churn—form of ball mill. The colour ought to be an impalpable powder, and bright lustrous varnishes are preferred to those made from copal and shellac. The grinding is sometimes done with only a portion of the varnish, and it is afterwards thinned down with the remainder. The pigments used for spirit varnish enamels are very numerous, viz. lampblack, ultramarine, blue, chrome green, vermilionette, etc., etc. Zinc oxide should not be used with methylated spirit varnishes as it forms zinc resinates and thus decomposes the methylated spirit varnishes. For the same reason red-lead should not be used as it solidifies in a few days. But zinc oxide can very well be used in spirit varnishes with turps or white spirit as the solvent, as in enamels with dammar varnish as the vehicle.

Hot Process.—To shorten the time occupied in the process of solution of the resin the solvent can be affected by the aid of heat. If the solvent be not too volatile, e.g. alcohol, the operation may be conducted in a glass flask, the lower half of which dips into a water-bath being kept in position by the usual rings. The flask must be shaken to hasten solution and economize solvent. In the case of intractable resins, e.g. copal and some kinds of Manila, the naked fire must be resorted to, but great care must be taken to prevent the mixture taking fire. Varnishes made by the aid of heat are more brilliant, but they are darker, and do not bind so well as those made in the cold. To prevent loss of very volatile solvents, Andes uses a cylindrical digester with a diameter about equal to its height, enamelled inside, resting upon a tripod placed in a water-bath K, which narrows at the top so as to catch hold of the digester ; the mouth of the digester is provided with a flange S, to which the lid is fastened by bolts, and only after the previous insertion of an india-rubber or leather washer. A shaft carrying a mechanical agitator R passes through the lid, and a tube AB carries the evolved vapours to a condenser F placed above the digester in such a manner that the condensed solvent falls back into the digester. With spirits of turpentine, coal-tar naphtha, or petroleum spirit the water in the bath is heated to boiling; in the case of chloroform, carbon disulphide, and wood-spirit the heat should not exceed 50° C., whilst in the case of ether and petroleum

ether and gasoline 40° C. should not be exceeded, care being taken at the same time to add a little ice to the condensed water to ensure complete condensation. This plant can also be used to thicken spirit varnish by collecting the condensed solvent apart instead of returning it to the digester. When working on the large scale, and also when using very volatile solvents, regular extraction plant may be employed similar to that used for fat extraction by solvents on the larger scale, consisting, for instance, of three large canisters one above the other. The solvent is heated in the first canister, the evolved vapours led to the top canister where they are condensed, the condensed liquid running down into the middle canister in which the resin to be dissolved is placed; finally the solution runs back into the first canister, where the solvent again distilled off reascends to the top canister to be again condensed and falls into the middle one, and so on until complete solution is effected. The advantage of the plant is that large quantities of very intractable resins may be dissolved with a minimum of solvent. Its compactness also enhances its value. Plant working on the same principle as that shown in Vol. II of this treatise (p. 25), may also be advantageously employed in the case of copal and amber. In that case the resin is fused before extracting it with turpentine. There is no loss of solvent.

TABLE XCV.—CLASSIFICATION OF SPIRIT VARNISHES ACCORDING TO PREDOMINANT RESIN AND SPECIAL USE.

Varnish.	Specially adapted for
Amber	Metals, photography, bookbinding.
Copal (fused)	Bookbinding.
„ (soft)	Interior decoration.
Dammar	Interior decoration, and objects not much handled.
Shellac	Articles subject to wear and tear, toys, leather, cardboard, blackboards, french polish.
„ bleached	Colourless varnishes.
Mastic	Toys and turned articles, pictures, cardboard, golden lacquer.
Sandarach	Pounce cabinet work, water-colours, visiting cards, varnish to be used to thin down colours, golden lacquer, white spirit varnish, wood-carving, metal plate work, photographic negatives.
Rosin, etc.	Poor quality picture varnish, etc.
Asphaltum	Varnish to be used as a vehicle for colours, metals.
Caoutchouc Gutta-percha	Flexible articles, electrical insulation, photographic negatives, waterproof varnishes.
Celluloid	Coloured varnishes and for same purposes as india-rubber and gutta-percha varnishes.

Storing of Spirit Varnish.—Spirit varnish must be stored in air-tight vessels constructed of a material that will not darken the colour of the varnish.

CHAPTER XXII.

AMBER, ASPHALTUM, COLLODION AND CELLULOID VARNISHES.

I. *Amber Spirit Varnishes.*—As seen in Volume II, amber is insoluble in all varnish solvents until after previous and appropriate fusion. But amber so fused (it must be kept in fusion until it has lost about 20 per cent of its weight) is much softer than natural amber. The resulting varnish is therefore somewhat tacky. Fused amber, or pyrosuccin, is never used alone in varnish-making, except in the case of photographic varnish, where its transparency and resistance recommend it. The usual solvent in that case is chloroform. Sometimes 22 parts of fused amber are dissolved in 14 parts of spirits of turpentine, but that varnish dries much more slowly. In many cases the fused amber is associated with a resin which will impart elasticity to the varnish. For example, 10 to 15 lb. of fused amber are dissolved in 15 lb. of spirits of turpentine according to the quality of the amber, and 1 lb. of Venice turpentine added. In ordinary spirit varnish sandarach is added, but the varnish is more brittle. The addition of mastic, elemi, or Venetian turpentine gives more elastic varnishes. The following formula is in very general use: Fused amber 4 lb., sandarach 4 to 6 lb., mastic 1 lb., Venetian turpentine 1 lb., methylated spirit 1½ to 3 gallons, according to whether a dark or pale varnish is required. Often a little camphor, say ½ lb., is added to facilitate solution.

II. *Asphaltum Spirit Varnishes.*—The best solvent for asphaltum is spirits of turpentine, and the best asphaltum is Syrian asphaltum. Coal-tar naphtha (solvent naphtha) may replace the spirits of turpentine, and the Syrian asphaltum may be replaced by a less costly pitch, stearine pitch, bone pitch. The coat produced by a pure asphaltum varnish if brilliant is brittle. Elasticity may be imparted to it by gum thus, or if cost is no object, by elemi or copaiba balsam or by a small quantity of a solution of india-rubber in coal-tar naphtha; by adding a very small quantity of castor oil a slower-drying varnish is obtained, but much more flexible. It is advisable to add two gallons spirits of turpentine to every cwt. of asphaltum to be fused so as to hasten the fusion. Asphaltum could very well be dissolved in a suitable solvent, say turps, in a revolving cask or barrel resting on trunnions, along with, say, 25 per cent of rosin and 5 per cent of manganese resinate previously fused and dissolved in turps. But independent of the fact that a special revolving barrel would

have to be kept for this purpose alone, there is another drawback incidental to this style of working. All the water in the asphaltum, resins, etc., goes into the varnish, causing it to lose its lustre and become dry, dull, and unsatisfactory. Cheaper varnishes are made by dissolving 4 lb. of coal-tar and 2 lb. of Stockholm tar in 1 gallon of coal-tar naphtha. Asphaltum or other pitch may be replaced by rosin, without, however, going beyond one-half the quantity of asphaltum usually employed.

TABLE XCVI.—MIXED ASPHALTUM SPIRIT VARNISHES.

	lb.	lb.	lb.	lb.	lb.
Rosin	5	10	7	5	5
Asphaltum	15	10	13	15	10
Spirits of turpentine	34	32	32	—	—
Benzol	—	—	—	30	32

Manufacture of Asphaltum Varnish.—Fuse together 50 lb. of finely powdered asphaltum and 25 lb. of rosin over a gentle fire, and add oil of turpentine to a consistency fit for the brush. In the meantime dissolve 100 lb. Manila copal, 100 lb. sandarach, and 50 lb. mastic in 1500 lb. of spirit. Mix the solution with some Venice turpentine, and add to the still hot asphaltum rosin mixture. Allow the whole to cool, and thin then with turpentine if necessary. The surfaces on which the varnish is to be applied must be perfectly clean and dry. The varnish should be applied to warm surfaces in a warm room.

Photographer's Asphaltum Varnish for Etching.—Asphaltum of Judea 8 lb., yellow wax 13 lb., benzol 15 lb. Dissolve and filter, decant on settling. The above solution is so limpid that it is used with albumen thinned with collodion and dries very strongly.

Varnish for Engraving on Glass: (1) *Winter.*—Dissolve 5 oz. of asphaltum in 100 fluid oz. of a mixture in the ratio of benzine 2 fluid oz., chloroform 1 fluid oz. (2) *Summer.*—Dissolve 5 oz. of asphaltum in 100 fluid oz. of a mixture in the ratio of chloroform 1 fluid oz., benzene 3 fluid oz. (3) Another formula: Dissolve 5 oz. of asphaltum in 100 fluid oz. of a mixture in the ratio of benzine 9 fluid oz., asphaltum 1 fluid oz. (4) Benzine 100 fluid oz., essence of lemon 10 fluid oz., asphaltum 5 oz., or (5) benzine 100 fluid oz., essence of lemon 10 fluid oz., asphaltum of Judea 6 oz., rectified spirits of turpentine 40 fluid oz.

Mordant for Etching on Glass.—Spirits of turpentine 100 fluid oz., paraffin 15 fluid oz., rosin 5 oz., white wax 5 oz.

Resist Varnish for Etching on Glass in an Acid-bath.—Asphaltum 20 oz., spirits of turpentine 60 oz., white spirit 40 oz., or paraffin wax 40 oz., yellow wax 40 oz., vaseline 20 oz. Applied by heating the whole plate to a sufficient temperature by a sufficient number of

TABLE XCVII.—VARIOUS ASPHALTUM COMPOSITIONS FOR USE IN ETCHING, PHOTO-ZINCOGRAPHY, COPPER-PLATE WORK, ENGRAVING ON STONE, ETC. (VALENTA).

									Solvents.						
No.	Asphaltum.	Common Rosin.	Dragon's Blood.	Mastic.	Shellac.	Fat and Oil.	Wax.	Soap.	Turps.	Benzol.	Chloroform.	Lavender Oil.	Lemon Oil.	Linseed Oil.	Remarks.
1	10	20 Rosin	—	—	60	—	—	—	—	—	—	—	—	—	Dusting powder for metal etching.
2	10	—	—	—	—	—	1	—	—	—	—	—	—	—	Ditto, photo-zincography with transfer paper, A. Albert.
3	2	2 Rosin	1	—	—	—	—	—	—	—	—	—	—	—	Ditto, metal etching, K. W. Pope.
4	60	15 Burgundy pitch, 25 Rosin	—	—	—	—	—	—	—	—	—	—	—	—	Ditto, Ditto (H. Calmanus, "Photo Chronik," 1891, pp. 15, 41).
5	40-50	—	—	—	—	—	—	—	—	1000	—	1	—	—	Solution for coatings sensitive to light. Pure or sulphuretted asphaltum may be used.
6	4	—	—	—	—	—	—	—	—	1000	—	—	3	—	Ditto.
7	200	—	—	—	—	—	—	—	—	1000	3000	7	—	—	Ditto, for direct copying process on stone.
8	10	—	—	5	—	—	—	—	—	300	300	—	—	2	Surface varnish for Bartos' process.
9	10	—	—	—	—	—	—	—	50	50	—	—	—	—	Fat ink for stone in asphaltum illustration.
10	20	—	—	—	—	2 Olive oil	—	—	50	25	10	—	—	—	Tincture for direct drawing on zinc plates.
11	10	10 Rosin	—	—	—	—	50	—	—	—	—	—	—	—	110 parts dissolved in turps to blacken the gelatine copy for photo-lithography.
12	20	60 Burgundy pitch	—	—	—	10 Palm oil	10	—	—	—	—	—	—	—	Transfer colour.
13	20	100 Rosin	—	—	—	140 Tallow	20	30	—	—	—	—	—	—	200 parts elemi, 60-80 parts varnish, 80-100 parts lampblack, Kampmann's ink.
14	40	30 Burgundy pitch, 20 Rosin	15	—	—	—	50	—	—	—	—	—	—	—	Etching basis.
15	20	2 Rosin	—	—	—		10	—	—	—	—	—	—	—	Etching basis for metal (Jeep), "Nothling der Asphalt," 1899, s. 280 *et seq.*
16	55	30 Rosin	—	90	—	15 Tallow	180	—	—	—	—	—	—	—	
17	4	2 Rosin	—	—	—	—	4	—	—	—	—	—	—	—	
18	500	200 Venice turpentine	—	—	—	120 Tallow	150	—	3000	250	—	—	—	—	50 parts coal-tar, 250 printing ink, Burian's asphaltum tincture, "Mittlg d. Nult geog. Inst. Vienna," p. 617
19	500	—	—	—	—	125 Tallow	125	—	3000	—	—	20	—	—	Asphaltum tincture, "Allgem. Anzeiger für druckeiem," 1900, p. 617.
20	6	4 Rosin	—	—	—	—	5	—	50	—	—	a drop	—	—	C. Cluth's (Halle a S.) asphaltum tincture, "Ratgeber für die gesamte Druck industrie," 1898, No. 26.
21	15	—	—	30	—	—	46	—	—	—	—	—	—	—	Surface varnishes for copper-plate work and etching. See H. Kohler, "Chemie der Asphate," p. 219, and W. Jeep, "E. Nothling der Asphalt," p. 280. No. 23 contains 30 grammes of amber in addition to the other ingredients.
22	15	—	—	30	—	—	30	—	—	—	—	—	—	—	
23	60	—	—	30	—	—	120	—	—	—	—	—	—	—	
24	20	Rosin	—	—	—	—	10	—	—	—	—	—	—	—	
25	11	—	—	18	—	3 Tallow	36	—	—	—	—	—	—	—	
26	40	10 Burgundy pitch, 20 Rosin	—	—	—	—	40	—	—	—	—	—	—	—	

lamps to heat it uniformly all over. The following liquid varnish can be applied by the brush: Spirits of turpentine 100 oz., spermacetic 10 oz., paraffin wax 15 oz., bitumen of Judea 10 oz.

Asphaltum Varnish for Wooden Vessels.—Two hundred parts of asphaltum are dissolved in 900-1000 parts of turps at moderate heat, and followed by 100 parts of elemi, 100 of yellow wax, and 100 of Venice turpentine, the whole being gently boiled for a quarter to half an hour, and strained through a cloth when cold.

TABLE XCVIII.—ETCHING GROUNDS.

Wax	30	38	30
Asphaltum	30	30	30
Rosin	15	—	—
Yellow pitch	7	30	15
Turpentine	—	15	—
Black pitch	—	—	15

TABLE XCIX.—ETCHING GROUNDS.

Asphaltum	50	100	100	5	4
Wax	5	—	—	6	8-12
Stearic acid	—	—	—	6	—
Yellow wax	—	20	10	—	—
Dammar varnish	15	—	10	—	—
Mastic	—	—	—	—	1·5-6
Potassium bicarbonate	5	—	5	—	—
Sodium carbonate	—	—	—	2	—
Rosin	—	15	15	—	2
Tallow	—	—	—	—	0·4-1
Venice turpentine	—	15	—	—	—
Black varnish	—	5	—	—	—

1. *A Varnish claimed to protect Iron from Hydrochloric Acid.*—Seven and a half lb. asphaltum, 5 lb. rosin, ½ gallon rosin oil.

2. *Varnish for Microscopic Work.*—Linseed oil 22½ oz., asphaltum 40 oz., turps 80 oz.

3. *Surface Varnish for Etching.*—Chloroform 200 oz., mastic 5 oz., asphaltum 10 oz., benzol 300 oz., paraffin wax 2 oz.

III. *Collodion Varnishes.*—Collodion or pyroxylin varnishes are very extensively employed and for very varied purposes. The more so as a great flexibility may be imparted to it by the addition of 2 parts of castor-oil. The solvent usually employed is the mixture of alcohol and ether: 1 lb. of collodion in 3 lb. of alcohol and 18 lb. of ether. For photographic purposes 1 lb. of collodion is dissolved in 1 lb. of alcohol and 1½ lb. of ether.

The addition of 25 per cent of carbon disulphide or benzol produces products of different colour and brilliancy.

The collodion ought to be perfectly dry, and to effect this it is placed underneath a bell-jar over sulphuric acid for about forty-eight hours. The solvents if miscible with water should be dehydrated.

Camphor to the extent of even 50 per cent is often added to the collodion. The mixture of alcohol and ether is often replaced by other liquids, such as acetone, wood-spirit, amyl acetate.

Acetone yields opaque varnishes analogous to that obtained by adding camphor; wood-spirit has the same effect when it contains acetone in appreciable quantity.

When acetate of amyl is used, in which collodion dissolves very easily, a bright colourless transparent varnish is obtained; moreover, the coating is much more malleable than that yielded by the ordinary solution. This is how the varnish so widely known under the name of "zapon" is made. "Zapon" spreads evenly over glass and gives a more homogeneous coating than other collodion varnishes; on the other hand, it dries more slowly owing to the high boiling-point of the amyl acetate.

Valenta proceeds as follows: 150 parts of nitro-cellulose are dissolved in 1000 parts of acetone, and there is then added 2000 parts of acetate of amyl and 2000 parts of benzine: the solution is clarified by decantation and filtration. This varnish yields a supple adherent coating which does not shell off. Finally, it has been proposed to impart to wood a coating of collodion varnish, i.e. to prime it with collodion and then to cover this coat which has filled up the pores of the wood with different varnishes which then become very lustrous, thanks to the layer of collodion, without either requiring rubbing or polishing.

It is also with collodion that the numerous compositions, known as "non-oxidizable bronzes," are prepared, thus: 5 parts of collodion are dissolved in 95 parts of acetyl acetic ether, and 25 parts of powdered bronze are then ground up in this solution; then to hinder the decomposition of the nitrated product 25 parts of dammar are dissolved in 75 parts of acetate of amyl.

TABLE C.—HALLE'S COLLODION VARNISH.

Amyl acetate	4 gals.
Benzol	4 „
Pyroxyline	2½ lb.

Farner dissolves nitro-cellulose in a mixture of amyl acetate and amyl alcohol.

TABLE CI.—FARNER'S NITRO-CELLULOSE VARNISH.

	I. lb.	II. lb.
Nitro-cellulose	100	100
Amyl acetate	150	400
Amyl alcohol	150	400

Elastic Varnish for covering the layer of collodion of the positive on glass in photography applied to curved surfaces, cameos, cups, saucers, etc.: Chloroform 30 oz., gutta-percha 1 oz.

Collodion Varnish for Negatives.—Ether of 62° B. 50 oz.

alcohol of 40° B. 30 oz., pyroxyline 2 oz. If the size small, ether 100, 90 per cent alcohol 100, nitro-cellulose 3.

Sensitized Collodion.—Alcohol 40° B. 50 oz., ether of 62° B. 50 oz., nitro-cellulose 1, cadmum iodide 0·5, ammonium iodide 0·5, cadmum bromide 0·25.

IV. *Celluloid Varnishes* are colourless, brilliant, adherent, do not crack nor rupture, and may easily be coloured by running in, whilst stirring, solutions of aniline dyes in very strong alcohol. They thus possess all the admirable qualities desired in a varnish, and may be rendered very elastic and more adherent by adding an oil soluble in the usual celluloid solvents, e.g. castor-oil. They thus find an ever-extending use as paper varnishes and for use on all the various articles in which lustre, durability, and transparency are requisite. They are more tough than collodion varnishes, and even a thick coat does not shell off, whilst collodion varnishes have to be applied in thin layers. Coats of celluloid varnish as thick as $\frac{1}{8}$ of an inch are quite brilliant and adherent. The celluloid should be dried perfectly before attempting to dissolve it by placing it in, say, a bell-jar over concentrated sulphuric acid. The solvents if miscible with water should be dehydrated. Celluloid requires the same solvents as collodion, viz. (1) a mixture of alcohol and ether, or (2) pure acetone, or (3) acetone and amylic alcohol, so that the varnish may dry more slowly, or (4) amyl acetate which gives a varnish like zapon. Amyl acetate if costly gives fine clear solutions of nitro-cellulose, but it dries slowly. If a mixture of amyl acetate and acetone be used "photographer's crystal varnish" results, which, applied cold, gives a transparent coat. By adding a little of a varnish resin a more dull layer is got better able to support retouching. Wood-spirit is cheap, and containing both methyl alcohol and acetone is a useful solvent. In applying celluloid varnish on collodion a few drops of water are added to the varnish to prevent it from dissolving the layer of collodion.

The following is claimed by a German writer as the best method of preparation: Chop thin sheets of celluloid, which are now procurable everywhere, into small pieces. Then put them into a large vessel with a mixture of methylated spirit, with quarter of its volume of ether, close the vessel airtight, and allow to macerate for a few days, shaking several times daily. The celluloid first swells up, and finally dissolves to a colourless liquid, which may be obtained of any consistency from a thick syrup downwards by regulating the quantity of solvent. The varnish is applied in thin coats with a wide brush. It is an excellent application for fabrics, as it not only waterproofs them but gives them a high degree of lustre. It even improves the lustre of silk. The varnish is also used with great advantage on wax-cloth, leather, or linoleum. The retention of the elasticity depends upon the very slow rate at which the camphor evaporates from the varnish coats, but if a little castor-oil or other non-drying oil is mixed with the varnish before use, the oil will preserve the elasticity even after

the camphor has all departed, and nothing is left of the original celluloid but the brittle nitro-cellulose. It is obvious that enough oil to prevent the varnish from drying is inadmissible. Of castor oil 2 per cent reckoned on the volume of the whole varnish is about the right amount. Celluloid varnishes are not inferior to the best copal varnishes, and much cheaper. They can be dyed any desired colour with aniline dyes.

The following method is said to be in use in France: Instead of rolling and drying the celluloid slowly the moist mass is run into an airtight vessel from which the air is exhausted by an air-pump so that the alcohol and excess of camphor evaporate rapidly and leave the celluloid in a spongy condition and so prevent collapse into a compact condition. *Formula.*—Spongy celluloid 100 lb., pure acetic ether 200 lb., sulphuric ether 25 lb., castor oil 5 to 10 lb., spirits of turpentine 15 to 25 lb., methylated spirits 75 lb., amyl acetate 1 lb., glacial acetic acid 20 lb. The acetic ether and acetic acid are mixed together, and after a time the celluloid is added. The mixture is agitated for six hours with fifteen minutes interval every hour. After a further six hours the sulphuric ether is added followed by the castor oil dissolved in a portion of the alcohol, the whole shaken up until completely mixed. The oil of turpentine, amyl acetate, and remainder of the alcohol are incorporated in turn, the order named being essential to success. The acetic acid and amyl acetate improve adhesion on undried articles, and the varnish is far richer in celluloid than those prepared in the ordinary way with greater resistance to acids and atmospheric influences. The articles to be coated must be gently warmed or the film will not look well, but it may be adapted for cold application by increasing the acetic acid by 40 lb. and the amyl acetate by 30 lb.

Waterproof Nitro-cellulose Varnish.—Kraemer and Van Elsberg make a waterproof varnish for paper by dissolving 100 parts of nitro-cellulose in a mixture of 450 parts of alcohol and 350 parts of acetone, the solution being then mixed with 60 parts of dichlorhydrin and 25 to 30 parts of plastal (ethers and amido derivatives of aromatic sulphonic acids). The product is applied to the surface of the material (e.g. paper) to be coated, and after being left a short time to dry, is subjected to moderate pressure under plates to impart a gloss.

Uninflammable Glaze for Paper, etc.—A preparation possessing the same gloss as stoved enamel and celluloid, but free from the inflammability of the latter, is manufactured by L. Degorce from the following ingredients: Alcohol 80 c.c. commercial photographic collodion 20 grammes, shellac 100 grammes, the latter being the essential component, whilst the alcohol acts as solvent and the collodion as adhesive. The resulting viscous liquid is applied to a sheet of glass of the same dimensions (width at least) of the paper or fabric to be coated. The latter is first surfaced with an adhesive of the following composition: Water 1000 c.c., glycerine 5 c.c., shellac 30 grammes, borax 40 grammes, formalin 2 c.c. Thus pre-

pared the paper or fabric is laid face downward on the layer of composition on the glass, and is rubbed or rolled into contact with same. After having been left long enough to become dry, the paper, etc., is detached from the glass by the ordinary means, and will be found coated with the glaze. An addition of 100 grammes of gelatine can be made to the adhesive.

TABLE CII.—CELLULOID VARNISH (TESCHENSCHNER).

Pyroxyline	3-4 lb.
Boracic acid	1 ,,
Rosin	25 ,,
Colouring	50 ,, in alcohol.
Ether alcohol	100 ,,

TABLE CIII.—NOBEL'S MIXED SOLVENTS FOR CELLULOID VARNISHES.

		Parts.			Parts.
A	Nitrocumol	5	F	Nitrated rosin soap oil	1
	Mononitronaphthaline	3		Nitrocumol	1
B	Nitrocymene	1		Mononitronaphthaline	1
	Nitrotoluol	1	G	Bromonitrotoluol	1
	Mononitronaphthaline	1		Mononitronaphthaline	1
C	Bromocamphor			Nitrocumol	2
D	Chloro or bromonitrotoluol			Nitrated rosin soap oil	2
E	Chloro or bromonitrocamphor				

TABLE CIV.—FORMULA FOR CELLULOID VARNISHES.

	I. lb.	II. lb.	III. lb.	IV. lb.	V. lb.
Celluloid	5	10	5	5	5
Amyl acetate	16	30	—	50	25
Acetone	16	30	—	—	25
Ether (sulp. meth.)	16	30	—	—	—
Camphor	—	4	5	—	—
Alcohol	—	—	50	—	—

Pollock has patented a nitro-cellulose varnish which when deposited on any object forms, he claims, a coating of more or less thickness, analogous to a skin, which is absolutely impermeable and is not apt to scale off or be deteriorated by the influence of the atmosphere or of water. He claims this product will replace advantageously the varnishes now in use in painting, marine work, coach-building, railways, shop fronts, etc.

It is composed of the following ingredients :—

TABLE CV.—POLLOCK'S CELLULOID VARNISH.

Acetone	300 parts by weight.
Acetic ether	100 ,,
Sulphuric ether	50 ,,
Camphor	100 ,,
Gum lac	50 ,,
Nitro-cellulose	200 ,,
Nitrated paper (dissolved in sulphuric ether)	100 ,,
Mastic in drops	100 ,,
	1000 grammes.

These proportions are not absolute, and may be varied according to their applications. The paper is first dissolved in sufficient sulphuric ether for that purpose without application of heat, after having been broken up by means of any appropriate apparatus. The cotton is dissolved in the same manner in the acetone, then all the other materials mentioned above are mixed with these two solutions in the same vat and well mingled by means of a stirring-rod. The product so obtained is applied in the same way as other varnishes, usually by means of a brush, upon the object to be protected, and forms a true pellicle or protecting skin, which will not crack or peel off, and which is absolutely impermeable. Pollock claims this varnish protects against humidity, whether the object be of wood, metal, or other material.

Coloured Celluloid Varnishes.—These are much in request for picturesque scenic illumination, for the bulbs of incandescent lamps, illumination bucket lamps, limelight and stained glass displays, foil papers, metallic capsules, artificial flowers, tin and metal work decoration generally. The basis varnish consists of: 24 lb. amyl acetate, 5½ lb. acetone, 4 lb. methylated spirit, 18 oz. celluloid chips.

Method.—Pour the acetone over the celluloid chips in a large jar, and bung down closely, as acetone is very volatile. After a few days complete solution is effected, and a clear jelly-like mass results; this is then diluted with the amyl acetate, and then the spirit is stirred in, the colouring matters having been dissolved previously in the latter. The solution is then strained.

In the making of enamel for steel, 4 oz. extra celluloid are necessary to bind the metallic powders, and this one may be made to serve a double purpose by being put up as an aluminium cycle enamel. The varieties and quantities of colouring are as follows:—

TABLE CVI.—COAL-TAR COLOURS FOR CELLULOID VARNISHES.

Amber	4	oz. spirit amber.
Orange	3½	,, ,, orange 13277.
Scarlet	4½	,, ,, scarlet R.
Yellow	4	,, ,, yellow M.
Mauve	1	,, ,, heliotrope 3 B.C.
Stage blue	2	,, ,, blue B.V.
Ruby	4	,, ,, ruby.
Moss green	4	,, ,, moss green 13196.
Pale brown	2¼	,, ,, brown A.
Deep blue	4½	,, ,, dark blue.
,, rose	3	,, ,, ,, rose (rose Bengal).
Pale green	2¼	,, ,, grass green 9366.
Dark brown	4½	,, ,, brown 13166.
Rose pink	1¼	,, ,, rose Bengal.
Gold	2	,, ,, gold Y.C.B.
Deep green	4	,, ,, dark green.
Steel	6	lb. aluminium "bronze," 2 lb. silver do.
Navy blue	3½	oz. spirit dark blue.
Fire red	4½	,, ,, poppy 13023.
Petunia	2¼	,, ,, violet 3 B.C.

It is much the best to make each colour separately in this

manner than by appropriate mixtures of the primary colours, owing to the difficulty of getting the mixed anilines to blend perfectly in the varnish.

Dead Black Celluloid Varnish for Wood.—A cheap and excellent dead black can be given to wood by the following process: The wood is planed and then glass-papered until all marks left by the plane-iron are obliterated, and the surface is left as flat and uniform as possible. It is then stained with a solution of nigrosine in about 75 times its weight of methylated spirit or wood-spirit. Two applications of this are necessary to give a good backing to the black varnish afterwards applied, and the first coat of nigrosine must dry thoroughly before the second is put on. Each application of stain must be followed by sand-papering to retain the smoothness of the surface. The stain is put on with a sponge or a brush according to the extent of surface to be covered. When the last coat of stain is ready a black varnish is applied warm (at about 25° C., equal to 77° F.). The varnish is made from the following recipe: Soften 30 oz. of celluloid in 60 oz. of very strong alcohol. Then dissolve in 675 oz. of acetate of amyl, and colour the filtered solution with 4 oz. of nigrosine and 15 oz. of lampblack. The lampblack must be rubbed up separately with a portion of the solution, which is then mixed with the rest. This varnish is applied, always in one direction, by means of a brush. If the wood has been properly primed with stain two coats will be sufficient.

Universal Bronze Lacquer.—Equally suitable for boots and leather goods as for application on iron, stone, glass, paper, cloth, and other surfaces. The inexperienced should note before making this liquid that it does not give a yellowish bronze like gold paint, but a darkish iridescent one, and is a pleasing variation in aids to home decoration. Some pretty effects are obtained by using a little phloxine instead of part of the violet aniline, or phloxine alone will produce a rich reddish bronze, and a lustrous peacock green is obtained with brilliant green crystals. Quantities: 1 gallon flexile methylated collodion, 1 lb. methyl violet. Mix, stand away for a few days to allow the methyl violet to dissolve, and stir frequently, taking care to bung down securely as the collodion is a volatile liquid, then strain and bottle off. It is applied with a brush, dries rapidly, and does not rub off or peel.

Transparent celluloid chips or waste cuttings may be readily obtained of most makers of nitro-cellulose compounds, the price usually being tenpence a pound, but, naturally, this will vary with the quantity taken.

CHAPTER XXIII.

COPAL AND DAMMAR SPIRIT VARNISHES.

V. *Copal Spirit Varnishes. Valuation of Copal.*—Copals are still always tested superficially and by physical methods. The value of copal is estimated simply by sieving it, and noting the relative proportions of large pieces, small pieces, and dust. The dust is inferior. But as copals are expensive, the small pieces and dust must be used, although impurities give much trouble in doing so. They contain plant debris, humus, clay, sand, bits of limestone, etc. The vegetable impurities are specially injurious in copal-running, as the heat carbonizes them, and makes the copal nearly black, a colour practically impossible to eliminate. Hence the copal is washed, to separate them. The dust is blocked or fused into lumps for use.

Impurities in small copal and copal dusts vary from ½ to 50 per cent. Organic impurities rarely exceed 5 per cent with an average of ½ to 2½ per cent. The large impurities are sand and earth. The practice of packing copal in bags causes much breakage and powdering in transit, and contamination with textile fibres from the bags.

As solvents for copal, in the determination of the impurities, ordinary spirit (96 per cent strength), propyl, butyl, and amyl alcohols, and the acetates (especially amyl acetate), oil of turpentine, oil of camphor, and ether, are all employed. The best solvents have the highest molecular weights. The best of all is amyl acetate, especially when free from water, and mixed with amyl alcohol, and nearly absolute ethyl alcohol. The best proportions are 20 to 25 oz. of amyl acetate, 40 to 50 oz. of amyl alcohol, and 25 to 40 oz. of high strength alcohol. Hot solutions of copal hardly admit of filtration, and an excess of solvent dissolves the copals less perfectly than the necessary amount. A concentrated copal solution is often precipitated by adding more of the solvent. The solutions may, however, generally be thinned with ether, so as to be just filterable. Another advantage of using as little solvent as possible is that the concentrated solution of the soluble resins acts as a solvent of the ones insoluble in the solvent used, so that they can be got into solution in this and in no other way. The same action is exerted on the insoluble constituents of copal by solutions of other resins. They are, for example, dissolved by a 10 to 20 per cent solution of rosin, and that solution is largely used for dissolving copals in the manufacture of linoleum and varnishes, and gives a more fluid and manageable solution than can otherwise be obtained.

To aid the tedious and often impossible task of filtering solutions of copal, it is best to keep them warm and allow them to settle, afterwards decanting the clear liquid. The harder and less weathered, i.e. the better a copal is, the more difficult it is to dissolve it, and the thicker and more gelatinous the solution is. The following process of testing is simple, cheap, and rapid, gives reliable results, and can be easily carried out in any works laboratory:—

Take a thin deep beaker holding about 4 oz., and tare it together with a glass rod. Then put into it 10 grammes of the copal, in the finest possible powder. Then add 50 c.c. of the above-mentioned mixture of amyl acetate, amyl alcohol, and spirit, and stir all the time with the glass rod to prevent the formation of any lumps. Then put the beaker on a water-bath and boil up its contents with constant stirring. Then cover up and allow to digest, with occasional stirring, for from thirty to sixty minutes. When all the copal is dissolved, i.e. when the undissolved residue is entirely loose, and shows no tendency to clot together, and when the glass rod is free from adhering resin, the clear solution is carefully decanted into a larger beaker. Rinse the insoluble residue two or three times with the solvent, and add the washings after settling to the clear solution. The solution is evaporated down and the residue weighed, the result being checked by weighing the insoluble residue, which consists of the impurities present in the copal.

Solubility of Copal.—The solubility of copals, generally, is summarized on pp. 46, 47 of Vol. II, and that of each copal under its own heading. The data given in Table XIV, and in Table on p. 202 of this treatise, Vol. II, are negative results, that is to say, Coffignier, in his data as to the solvent action of various volatile solvents on resins, unfortunately has chosen to give his results in a negative form, so that his tables, instead of showing the degree of solubility in a positive manner, are tables of degree of insolubility. It is unnecessary here again to go over the same ground anent such oil-varnish resins as are used in spirit varnish-making except to supplement what has been said in Vol. II, and to recapitulate one or two important points.

Attempts have been made to dissolve copal by two different solvents, so as to dissolve one part of the resin in one solvent, say, in methyl alcohol, and another portion of the resin in the second solvent, say, in acetone, by aid of heat and pressure. It has long been known that the vapour of camphoretted alcohol, etc., dissolves copal. Camphoretted ether (1 in 12) is a good solvent for both copal and pyro-copal. Another method depends on the fractional addition of alcohol. If warm alcohol be added in small portions at a time to the syrup obtained by warming copal in ether, many kinds, such as white and red Angola, kauri, and Manila are completely or, in great part, dissolved. By adding ½ per cent of sulphuric acid to alcohol an important addition to its solvent capacity is imparted. Formerly the benzol mixture, equal parts by volume of spirits of

turpentine, carbon disulphide, benzol, was prescribed as a mixed solvent for copal, but only some copals dissolve therein to any great extent, such as Congo, white Angola, and Manila copal, and the solution is turbid. In the presence of chloral hydrate the solubility of copal is greatly enhanced. Manila copal is to a great extent soluble in an 80 per cent chloral hydrate solution and kauri copal partly so.

If hard copals as a class be insoluble in alcohol, unless previously fused so as to lose by partial destructive distillation a certain percentage of their weight, varying not only with each class of resin, but with different samples of any given variety, yet, medium and soft copals dissolve, fairly freely, in their original raw condition, yielding pale, non-tacky varnishes. The softer the copal, the more readily does it dissolve. Manila and Borneo copals yield pale solutions with methylated spirit, which clarify quickly and leave, on application to a suitably prepared surface, a brilliant coat, but one apt none the less, more especially in the case of Manila copal, to "string" most inconveniently before drying. The coat can, in fact, before it is quite dry, be flayed off the surface on which it is applied like the young bark from the new shoots of a tree. Benguela, Angola, and Sierra Leone copal varnishes are not quite so bright because they require more alcohol (methylated spirit) to bring them into a state of solution.

This stringiness of Manila copal prevents it replacing shellac in French polish and debars it as an ingredient of polishing varnishes. According to Baringer, it has hitherto been impracticable to use relatively cheap resins like Manila copal and sandarach in place of the more expensive shellac for cabinetmakers' polish, because, even at the ordinary temperature, these resins combine with the oil used and form a sticky, greasy mass which prevents their being uniformly distributed over the surface to be polished in such an extremely fine state of division as can be done by adding a small quantity of oil to the alcoholic solution of shellac. He proposes, however, to overcome this difficulty by converting the resin in question into a condition in which they are insoluble in oil, so that they will then behave like shellac, and will polish with as small a quantity of oil as is needed for the latter. The treatment consists in intimately mixing the Manila copal, sandarach, or other resin soluble in alcohol, with 1 to 5 per cent of a fatty oil, and gently heating the mixture till it is sufficiently thickened. In this state it is maintained at the same temperature, with constant stirring, for half to one hour. This, says Baringer, makes the resins insoluble in oil, so that, after the solvent spirit has evaporated there remains a hard and non-tacky layer of varnish. But Baringer has hardly grasped the point. Manila copal is simply thrown out of its solution in the spirit varnish by the oil into a stringy mass. Whether his treatment, founded on a wrong principle entirely, is effectual is somewhat dubious; the solubility of Manila copal is greater in an alcoholic solution of rosin than it is in

pure alcohol, and that is the basis to work upon to stop stringiness, and the wrong principle of mixed solvents is well brought out in the case of Manila. When one of the solvents which keep the resin in solution by the mutual solvent action of itself and the other solvents is evaporated, the resin in the coat of varnish falls out of solution, the remaining solvents separate out from the resin and leave it to dry as a tacky, irregular layer, full of waves, sinuosities and punctuations. To touch it before it has dried thoroughly spells disaster from the stringiness of the coat. Mixed solvents, even when the resin dissolved is soluble in each, cause the varnish to dry irregularly from very obvious causes. For equally obvious causes the varnish dries still more imperfectly when the resin dissolved is soluble in neither of the component solvents but only in the mixture thereof.

If the tendency to string is not equally highly developed, yet neither do different samples of Borneo and Manila copals all dissolve equally freely. They often form in the varnish-making vessel a viscous mass which stringsstrongly and only dissolves but very slowly and very partially, always leaving a bulky insoluble residue. These kinds should not be bought, at any rate for spirit varnish purposes. The solubility in ordinary methylated spirit of any Manila copal intended to be used in spirit varnish-making, and its greater or less tendency to string on drying, is the great point which requires examination before buying any given lot of such copal or accepting delivery thereof. Some firms carefully test all samples before buying, but most irrationally forget to test deliveries to see if bulk corresponds with sample submitted and on which purchase was made, and it is only when a hitch occurs in the course of manufacture that the delivery is tested—when too late. The less freely soluble varieties of Borneo copal, Manila copal, and other hard, medium hard, and soft copals were recommended by the older writers on varnish-making to be freely ground and exposed to air for say a twelvemonth, when they were said to dissolve much more easily and leave a far less bulky residue. But why should the varnish-maker court additional labour which by skill in varnish-making and skill in buying he can avoid? Spirit-soluble Manila copal is what he wants, and he should see that he gets it. Venice turpentine, gum thus, Burgundy pitch, or elemi may be added to copal spirit varnishes to give elasticity, and it is good policy first to get a clear alcoholic solution of the oleo-resin and use that solution to dissolve the copal, as the alcoholic solution of the oleo-resin has got a greater solvent action on copal than methylated spirit by itself alone possesses. The recipes generally vary with the copal and the elasticity required, 3 to 5 lb. of copal to the gallon of methylated spirit with the addition of 1½ to 2½ lb. of Venice turpentine, Burgundy pitch, gum thus, or of common rosin. Medium hard but intractable copals must be previously fused, but not so far as to convert them into *pyrocopal*, as in oil varnish-making. After this treatment the roasted copal is more soluble in spirit: (1) 4 lb. of copal are melted at a

very gentle heat, and, when the resin is quite fluid, 2 lb. of Venice turpentine are added and well mixed. When the mass is quite homogeneous, it is run on to a glass plate, and when cool pulverized and dissolved in the water-bath in 1 gallon of methylated spirit; (2) 3 lb. of copal are gently fused and poured in a fine stream into much cold water. When cool, the water is run off and the well-dried copal mixed with 3 lb. of sandarach and 3 lb. of mastic, both finely pulverized and dissolved in the usual way in 2 gallons of methylated spirit, in which 2 lb. of Venice turpentine have been dissolved. 1. *Solution in Spirits of Turpentine.*—Only pyrocopal can be used (5½ lb. to the gallon), which gives a deep brown-coloured varnish. Camphor, rosemary oil, or cajeput oil, or some other camphoriferous essential oil, is often added to aid solution, but this softens the varnish, impedes drying, and renders it tacky. *A Very Durable Varnish.*—Dissolve by gently heating on the water-bath 3 lb. of pyrocopal, 2 lb. fused amber in 2½ gallons of spirits of turpentine; add 1 lb. Venice turpentine, and continue heat till homogeneous. Copal is, as just discussed, more soluble after prolonged exposure to air. Exposure to air and light, during process, further facilitates solution in spirits of turpentine. When a small quantity of copal is added to spirits of turpentine, and exposed to air and sunlight, the copal dissolves freely without heat. Spirits of turpentine is rectified so as to produce 90 per cent of rectified spirits, of which 480 parts by weight are run into a flask and 10 parts of finely ground copal added, the flask closed by a loosely fitting cork and exposed to air and light. Gradually the copal dissolves, and the solution is used to dissolve a larger quantity of copal. Some sorts do not dissolve. 2. *Solution in Acetone.*—Most copals dissolve partially in acetone (3 lb. to gallon). The varnish dries hard and brilliant. On driving off the acetone, the residual copal dissolves much more easily, and in a smaller quantity of acetone. 3. *Solution in Mixed Solvents.*—Copal contains several resins, each soluble in different menstrua. Hence the theory of mixed solvents. A single solvent dissolves a certain amount of copal, but there is often left a swollen intractable residue which it is the function of the mixed solvent to dissolve. 4. *Ether plus Alcohol plus Spirits of Turpentine.*—Mix 20 lb. of finely pulverized copal with 5 lb. of camphor, and add to 8 gallons of ether; let stand for twenty-four hours. It is run into a mixture of 2 lb. of spirits of turpentine and 2½ gallons of methylated spirit. The mixture becomes clear on stirring. It separates on standing, for several days, into two layers, the lower richer in copal and the upper poorer therein, and absolutely limpid. The top layer—an excellent varnish—is run off, and the bottom layer, still containing undissolved, swollen copal, again treated with camphoretted ether. Heeren says only pale, West Indian copal, with a smooth surface, colourless, with a rounded surface, and conchoidal fracture should be used, whilst East Indian (Zanzibar) copal, in small pieces, with a wrinkled surface and yellow colour should be rejected. The latter do not

dissolve, but form a gelatinous mass. [In other words, it is so far in vain to use an oil-varnish resin—only soluble after fusion—in spirit varnish manufacture and expect it to dissolve forthwith in the volatile solvent used.] The best proportions for the mixed solvent are alcohol of 98 per cent 6 lb., sulphuric ether 10 lb., spirits of turpentine 40 lb.; 60 lb. of copal dissolved in this mixture gave a varnish of the consistency of linseed oil. The copal does not swell nor gelatinize. Solution may be facilitated by the aid of a very gentle heat. The instructions for this class of work were often only applicable by amateurs. They were told, for instance, that the brightest and palest pieces should be selected; but as some of these might dissolve badly, it was best to try each lump separately by dropping it into a test-tube, containing a small quantity of the solvent. It ought to dissolve in a few minutes without gelatinizing. When the requisite quantity of copal which stood this test was obtained, the resin was dissolved and filtered if need be. A quick-drying, colourless, almost limpid varnish was obtained, but which like all turpentine varnishes was tacky for some time.

5. *Alcohol and Spirits of Turpentine.*—It has been pleaded that as Sierra Leone copal consists of a mixture of two resins, one soluble in spirits of turpentine, the other in alcohol, the most rational solvent for this resin is a mixture of these two solvents. Two lb. of finely pulverized Sierra Leone copal are added to 1 lb. of alcohol, stirring the mass until the resin, soluble in alcohol, is dissolved and the insoluble resin separates as a greyish-white gelatinous mass. The alcoholic solution is decanted and forms in itself an excellent spirit varnish. One and a half lb. of rectified spirits of turpentine are now added to the residual resin, and the whole stirred until completely dissolved. By mixing the two solutions an uncommonly good varnish is said to be produced. But this piecemeal style of effecting solution is not one which would commend itself to British varnish-makers. Be that as it may, Andes claims to have dissolved Manila, Borneo, Sierra Leone, and Benguela copals in this same mixed solvent, obtained by mixing equal proportions of alcohol and turps. But Zanzibar and Angola copals swelled without dissolving even by the aid of heat.

6. *Camphor, Alcohol, and Oil of Lavender.*—Four lb. of copal are finely pulverized with 1 lb. of camphor, 8 lb. of oil of lavender are added, and after 12 hours contact 15 lb. of 98 per cent alcohol.

7. *Spirits of Turpentine and Oil of Lavender.*—Five lb. of finely pulverized copal are dissolved in a mixture of 6 parts of oil of lavender, and 20 parts of spirits of turpentine.

8. *Alcohol and Acetone.*—Three lb. of pulverized copal are added to 6 lb. of acetone, and after twenty hours 10 lb. of 96 per cent alcohol are added. The solution is aided by gentle heating on the water-bath, and when complete ½ lb. of Venice turpentine is added. A very tenacious elastic varnish is thus produced.

More Complex Mixtures.—Finally, according to the object in view,

much more complex mixtures may be used as solvents. The use of a mixture of spirits of turpentine, wood-spirit, benzol, and carbon disulphide has already been indicated.

9. *Ether plus Acetone plus Chloroform.*—Similarly, Valenta used a mixture of 300 lb. of ether, 200 lb. of acetone, and 10 lb. of chloroform, and by aid of this mixed solvent prepared an excellent photographic varnish (negatives), giving a hard, durable coat by dissolving in this mixture 30 lb. of Angola copal, and 30 lb. of yellow amber debris. A part of these resins dissolve either in the cold, or after heating in an apparatus connected with a reflux condenser, and there is thus obtained a pale yellow, limpid fluid which gives a brilliant and transparent coating. Whilst recognizing the great advantage of these mixed solvents, it must be borne in mind that they do not act similarly with all varieties of copals. The published formulæ scarcely ever give the variety of copal that is to be used. It is therefore always necessary to make several preliminary trials on the sample of copal to be treated. Copal being an oil-varnish resin as well as a spirit-varnish resin, the general properties of which, including its solubility *inter alia* in spirit-varnish solvents, were described in Vol. II of this treatise (pp. 41-87), to which the reader is referred. He will do well to bear in mind that Coffignier's figures on pp. 67, 87, and 202 of Vol. II are negative or give insoluble per cent.

10. *Epichlorhydrin.*—So as to save time, economize labour, eliminate danger from fire, and prevent waste of the proximate principles which give hardness and durability to copal, further attempts have been made during the last decade to dissolve this intractable resin by the use of special solvents or special mixtures of solvents without the previous fusion and partial dry distillation of the resin, which must perforce take place before copal can of itself dissolve in linseed oil or in spirit varnish solvents.

The data as to the solubility of various copals in epichlorhydrin and dichlorhydrin have already been given in the chapter on solvents. These solvents were first applied to the solution of copal in its natural state in 1895 by H. Flemming. But the chlorhydrin process is defective in many ways, the chief drawbacks being the extravagant price of the solvents which puts them at once outside the domain of the practical politics of the varnish trade, besides the time lost in dissolving the copal by digesting it under a reflux condenser with the solvent, render the method still more impracticable. When to this is added the fact that the drying properties of the chlorhydrin varnishes are highly problematical, the process, it may be said, has little to recommend it. The ideal solvent for copal must not be too dear, it must really dissolve copal in the true sense of the word, and not merely hold it in solution, in a state of unstable equilibrium like a colloid jelly, ready to disgorge it as a tough, gelatinous, intractable mass on the very slightest inducement or provocation. If the solvent itself dissolve in linseed oil, then so also should the dissolved copal, or the so-called solution of copal

is no true solution but a solution exactly resembling one of colloid silica, more especially as regards instability. Moreover, for spirit varnish purposes the long-looked-for solvent must so dissolve copal that a film of the partially dried varnish should not be capable of being drawn off in long, whip-thong-like strings. In a word, the solvent required for copal must dissolve it and distribute it over a given surface with as great ease as alcohol does shellac and with as few technical drawbacks.

The following formula for chlorhydrin varnish may prove interesting :—

Chlorhydrin Varnishes.—One part of dichlorhydrin is poured on to 1 part clean and dry kauri and the mixture allowed to stand for some time ; then 1 part of methylated spirit added and the whole heated to complete solution. By the addition of 15 per cent of linoleic acid or castor oil a varnish is prepared which is paler than any other oil varnish. It is said to give, when applied to natural wood without use of filters, a quick-drying coat which can be rubbed down and polished with linseed oil.

11. *Amyl Alcohol as a Solvent for Copal.*—Although, according to Vogel, copal should be completely soluble in amyl alcohol, the hardest kinds may be immersed therein for years without being entirely dissolved. [See also this treatise, Vol. II, p. 46, under (7) Amyl Alcohol.] Livache, however, claims that the addition of a small quantity of nitrous acid to the alcohol will cause even the hardest copal to dissolve completely within three weeks. This solution is not precipitated by oil of turpentine ; and mixtures of the two can be separated by distillation. [Compare this treatise, Vol. II, p. 46, under Nitric Ether.] The mixture deposits an acid substance after a short time, but this can be eliminated by adding a little of a solution of potassium oxide in amyl alcohol. The addition of linseed oil to the solution of copal in turps gives a precipitate, but since the fatty acids of linseed oil retain the copal in solution, a good oil varnish can, it is claimed, be prepared in that way. For example, 1 part of copal in solution is dissolved in 2 parts of oil of turpentine and mixed with $\frac{2}{8}$ part of linseed oil and $\frac{3}{8}$ part of linseed oil fatty acids. This varnish dries slowly, but can, it is claimed, be made quick-drying by heating it for several hours at 130° to 140° C, with the addition of a little manganese rosinate. The product, it is claimed, is transparent and elastic.

Manufacture of Linoleic Acid for Spirit Varnish-making.—As formulæ involving the use of linoleic acid in spirit varnish-making are on the increase, the following method of preparation may prove useful:—

One hundred and fifty parts of old linseed oil are boiled by indirect steam in an iron pan with an equal weight of caustic soda lye (30° B.) until completely saponified, and heated further along with 750 parts of water until a clear solution is obtained. Meanwhile, 150 parts of water and 36 of sulphuric acid (168° Tw.) are heated

in a lead-lined pan, fitted with a leaden steam coil. This done, the soap solution is run into the dilute acid in a thin stream and boiling is continued until the supernatant layer of linoleic acid has clarified. It is then left to settle, the acid water being drawn off and the linoleic acid thoroughly washed with hot water, heating being afterwards continued till the fatty acid is clear and free from water. The product, which is soluble in spirit, is used up to 5 per cent for softening spirit varnishes, instead of the castor oil frequently employed for this purpose. It may also be used as a grounding for oil paint on fresh cement plaster, to prevent peeling; the plaster being washed over frequently with water, to remove the soluble alkali salts present, then allowed to dry, a coat of linoleic acid being applied and topped with paint when dry.

It may be as well to point out that Coffignier, as the result of special experiments, flatly contradicts the conclusions of Livache, anent the solubility of copal in amyl alcohol plus nitric acid. That is only to be expected, and proves once more the danger of generalizing from the solubility of one tiny fragment of a lump of resin in any given solvent or mixture of solvents. Had Livache repeated his experiments on another sample he also might have failed. Had Coffignier repeated his experiments on another sample he might have chanced to pick up a piece not only soluble in amyl alcohol plus nitric acid but in amyl alcohol alone. No two distinct pieces of copal even from the same delivery agree in their solubility in amyl alcohol, as anyone can prove for himself, as the writer did several decades ago.

12. *Terpineol as a Solvent for Hard Copals.*—We now come to terpineol copal varnishes. Tixier and Rambaud claim to prepare varnish from hard copals by simple solution, without previous melting. They treat oil of turpentine with nitric acid, in order to form terpineol ($C_{10}H_{16}O$), a very energetic solvent, which can be diluted with spirits of turpentine, benzol, alcohol, to reduce the cost. The solvent can be prepared by two different methods. In the quicker one the spirits of turpentine is stirred up with dilute nitric acid (density about 20° B.), specific gravity 1·162, and warmed to 60° to 70° C. (140° to 158° F.). The turpentine becomes dark in colour, increases in density, assumes a different odour, and becomes less inflammable. When the mixture no longer precipitates a solution of kauri in terpineol, the turpentine so treated is separated by decantation, washed with slightly alkaline water, and distilled with the aid of steam. The distillate is a pale liquid, consists of unaltered oil of turpentine, terpineol, and dehydration products of the latter, such as terpinolene, terpinene, dipentene, etc. As this method furnishes a product liable to vary in constitution and be dark in colour, the slower cold process is preferred. This consists in maintaining the mixture at a low temperature, viz. 15° to 20° C. (with the aid of a cooling mixture if necessary), during the action of the nitric acid on the oil of turpentine. Nearly

the whole of the latter is converted into crystallized terpine, which has then merely to be washed with water and transformed into terpineol by the action of very dilute sulphuric acid. The nitric acid used may be replaced by a mixture of sulphuric and hydrochloric acids, but the results are less satisfactory. The terpineol obtained by one or other of these methods is industrially pure, is optically inactive, and has the specific gravity about ·940, with the refraction index 1·4780 or over at 20° C. It dissolves the hard resins to a pale varnish, which may then be diluted with turps or spirit. When oil is used, the quantity that may be added varies directly with the amount of terpineol present and its degree of acidity, which latter property may be increased by adding soluble fatty acids, as neutral oils are apt to precipitate the resin from its solution in terpineol.

Copal Spirit Varnish, by Solution in a Single Solvent; Ether.—Attempts have been made to obtain a quick-drying varnish by dissolving copal in ether, but according to Violette, and contrary to the assertion of Tingry, copal does not dissolve directly in ether without being previously heated so as to drive off one-fourth or one-fifth of its weight. The fused or pyrocopal thus obtained is soluble in ether, but it is not so hard as the original copal and may even be tacky like fused amber. *Process.*—Five hundred parts of finely pulverized pyrocopal are run into a flask and 1000 parts of ether by weight gradually added, shaking after each addition; the copal rapidly dissolves, and after complete solution the whole is allowed to stand for some time and the clear liquid is filtered through linen or paper, taking care to prevent loss by evaporation in the manner previously indicated. Before using this varnish, which possesses a beautiful brilliant lustre, it is advisable to prime the surface to which it has to be applied with an essential oil, such as spirits of turpentine, oil of spike, rosemary oil, so that the varnish does not thicken too rapidly and the coating pit from the escape of enclosed ether.

TABLE CVII.—VARNISH FOR OPTICAL INSTRUMENTS.

	Parts by Weight.
Copal	10
Essence of lavender	50
Powdered camphor	1

Dissolve the copal and camphor in essence of lavender, then warm sufficient spirits of turpentine to obtain the necessary fluidity for the varnish, and add the mixture slowly to this.

TABLE CVIIA.—TERPINEOL COPAL VARNISHES.

	A lb.	B lb.	C lb.	D lb.	E lb.	F lb.	G lb.
Copal	20	20	50	80	50	50	50
Terpineol	10	9	40	20	40	25	40
Turps	20	—	—	50	—	—	80
Alcohol 95 %	—	25	60	—	150	75	—

A, B, C, D = Manila. E, F, G, Kauri.

TABLE CVIII.—MANILA, BORNEO, ANGOLA, BENGUELA, AND SIERRA LEONE SPIRIT VARNISHES.

1.	Manila copal	160 lb.
	Venice turpentine	40 ,,
	Methylated spirit	36 gals.
2.	Manila copal	160 lb.
	Burgundy pitch	50 ,,
	Methylated spirit	36 gals.
3.	Manila copal	50 lb.
	American rosin	30 ,,
	Burgundy pitch	30 ,,
	Methylated spirit	20 gals.
4.	Manila copal	50 lb.
	Australian sandarach	50 ,,
	Venice turpentine	30 ,,
	Methylated spirit	30 gals.
5.	Manila copal	50 lb.
	Australian sandarach	50 ,,
	American rosin	30 ,,
	Venetian turpentine	30 ,,
	Methylated spirit	31 gals.
6.	Borneo copal	140 lb.
	Venice turpentine	60 ,,
	Methylated spirit	40 gals.
7.	Borneo copal	140 lb.
	Burgundy pitch	70 ,,
	Methylated spirit	40 gals.
8.	Borneo copal	110 lb.
	Elemi	40 ,,
	Methylated spirit	33 gals.
9.	Angola copal	100 lb.
	Burgundy pitch	40 ,,
	Methylated spirit	22 gals.
10.	Benguela copal	100 lb.
	Burgundy pitch	50 ,,
	Methylated spirit	25 gals.
11.	Sierra Leone copal	100 lb.
	Venice turpentine	30 ,,
	Methylated spirit	12 gals.

TABLE CIX.—COPAL SPIRIT VARNISHES. PARTS BY WEIGHT.

Copal	10	20	60	75	50	36
Sandarach, Australian	—	—	—	150	50	74
Mastic	—	—	—	115	25	86
Venice turpentine	—	—	—	60	—	80
Seed lac	—	—	36	—	—	—
Rosin	—	—	25	—	—	—
Balsam of copaiba	—	2½	—	—	—	—
Spirits of turpentine	10	40	—	—	25	—
Alcohol	5	15	400	400	130	200

Extra White Label Varnishes.—1. Dissolve 20 lb. white powdered Manila copal and 10 lb. of white rosin in 20 lb. 96 per cent methylated spirit on the water-bath. Then filter.

2. As No. 1, except that the proportions are different, viz. Manila copal 20 lb., rosin 10 lb., spirit 25 lb.

3. As No. 1, with 15 lb. each of Manila copal and rosin, and 20 lb. of spirit.

4. As No. 3, but with 25 lb. of spirit.

5. As No. 1, but with 12 lb. Manila copal, 18 lb. rosin, and 20 lb. of spirit.

6. As No. 5, but with 25 lb. of spirit.

Coffin Varnish.—Dissolve 18 lb. of pale yellow rosin and 12 lb. of Manila copal in 25 lb. of 96 per cent methylated spirit on the water-bath. This varnish can be coloured brown or black with aniline dye.

Deep Black Spirit Copal Leather Varnish.—Take Manila copal, ground, 30 parts; sandarach, 1a, ground, 19; Venice turpentine, 5;

castor oil, commercial, 5; nigrosine, alcohol soluble, 6; alcohol, 95 per cent, 150 parts. Dissolve the sandarach and copal in 125 parts of the alcohol (in manufacturing on a large scale this is done in a revolving cylinder moved by appropriate machinery (Figs. 44-7)). Heat the Venice turpentine and castor oil (the sort used in the arts) together in a pot and stir till a homogeneous mixture is obtained, then add to the alcoholic solution of resins and stir well together. Warm the remaining alcohol on a water-bath to about 30° C. (86° F.), and in it dissolve the nigrosine. Strain the varnish through linen, and then add the solution of nigrosine and stir until homogeneous. Set aside for two weeks, and then carefully draw off into bottles or tins.

TABLE CX.—SPIRIT COPAL FOR PALE WOOD.

Copal	75 oz.
Mastic	13 ,,
Camphor	a little
95 per cent alcohol	100 oz.
Venice turpentine	6 ,,

Use sand-bath. Can be polished.

TABLE CXI.—SIERRA LEONE, BORNEO, AND MANILA COPAL SPIRIT VARNISHES. PARTS BY WEIGHT.

	lb.	lb.	lb.
Sierra Leone copal	—	—	10
Borneo copal	—	11	—
Elemi	—	4	—
Manila copal	16	—	—
Venice turpentine	4-5	—	3
Methylated spirit	30	27	10

Spirit Copal Varnish for Leather.—Seventy gallons of methylated spirit (95 per cent), 300 lb. of powdered Manila copal, 100 lb. of Venice turpentine, and 6 lb. of nigrosine or aniline black, soluble in spirit. The nigrosine is dissolved in 2½ to 3 gallons of cold spirit, the turpentine being dissolved in 8 to 10 gallons of the same solvent. The copal is shaken up in a barrel with the remainder of the spirit for three to four hours, then strained through a fine sieve, and mixed with the dissolved turpentine and dye. The preparation may be scented with a little oil of lavender, and should be stored in glass bottles. The smell (if any) of the spirit can also be masked with oil of cloves or mirbane. The same preparation can be made in other colours by using suitably coloured dyestuffs.

Uninflammable Liquid Spirit Copal Polish.—Beaumont proposes to render liquid polishes for flooring, furniture, leather, etc., uninflammable by an addition of carbon tetrachloride. The following proportions may serve as typical, though capable of modification, according to circumstances: Carbon tetrachloride 550 parts, oil of turpentine 225, beeswax 125, hard copal 10, and wood alcohol

90 parts. The beeswax is cut up into small pieces and placed, along with the carbon tetrachloride, in a pan that is heated on a water-bath to a temperature not exceeding 70° C., the mixture being stirred till all the wax is dissolved. The flame being extinguished, the turps is stirred in until a uniform mixture is obtained. Meanwhile the copal has been dissolved in the wood spirit, and the two solutions can then be mixed, the whole being well incorporated, especially as the liquid is being poured into the tins, etc., for sale. The preparation can be coloured or scented if desired.

VI. *Dammar Spirit Varnishes.*—Dammar spirit varnishes are inferior to spirit varnishes made from good sorts of copal. They are, however, superior to Manila copal in so far as they are free from the great fault of stringing so as to be capable of being flayed off in thongs when touched before quite dry. For certain purposes they are preferred on account of their lustre, moreover they are generally brighter and paler than amber or copal varnishes, but their great fault is want of durability and liability to surface drying when used in too viscous a solution, and in a highly volatile solvent. This quasi-dry surface layer covers a more or less solvent saturated layer beneath which out of doors melts with each rising sun and solidifies with each setting sun until it shows as many wrinkles and furrows as the bark of a pine hoary with the age of centuries. Rosin aggravates these defects. Dammar is essentially an indoor varnish.

Solution in Ether.—Though dammar is only partially soluble in ether the ethereal solution is used as a varnish, particularly as a picture varnish, on account of its lustre and transparency. It is necessary to work with dilute solutions, otherwise the rapid evaporation of the ether causes the formation of a superficial layer which hinders the varnish underneath from drying, thus doing away with any benefit derived from the use of a quick-drying varnish.

Spirits of Turpentine.—This is one of the best solvents for dammar. It dissolves therein completely in the cold, but it is preferable to work with the aid of heat, so as to drive off moisture which is present in large proportion, and which would otherwise yield a cloudy varnish; the heat should not, however, be so great as to darken the varnish. Venice turpentine is added to impart greater body and elasticity.

Process.—The Venice turpentine is melted in an enamelled, round-bottomed, cast-iron pan, 25 inches deep by 18 inches wide, and heated over a suitable furnace built into brickwork. The roughly-crushed and well-sifted dammar is then added, rejecting the powder which passes through the sieve, because it gives a deeper coloured varnish. The mass is well stirred and covered with a tight-fitting lid. The melting of the dammar takes from an hour to an hour and a half according to the quantity used. Towards the end, the boiling mass rises in the pan; the process has therefore to be watched carefully, and stirred with a wooden agitator. When the mass is completely fluid the pan is removed from the fire, and after

cooling the spirits of turpentine is added, at first a little at a time, whilst stirring slowly; when the mass is homogeneous the remainder is added. The resultant varnish is filtered through coarse linen and allowed to stand for several weeks to completely clarify. Sometimes the dammar is heated by itself, and to the melted mass deprived of its moisture the solid turpentine is added, and the operation continued as before. When it is not desired to add any solid turpentine it is best to add a little spirits of turpentine to the dammar at the beginning to prevent the resin from sticking to the sides of the pan.

The proportions generally used are 6 or 7 lb. of dammar to the gallon of spirits of turpentine. If solid turpentine be used the proportions for 20 parts of dammar vary between spirits of turpentine 22 to 32 parts, solid turpentine 4 to 20 parts, according to the body and elasticity desired in the varnish, the quantity of spirits of turpentine increasing proportionately with the solid turpentine.

To get a good-bodied varnish dammar requires its own weight of *spirits* of turpentine and half its weight of thickened turpentine, but if more than 2 parts of thickened turpentine to 1 part of the spirits required to dissolve the dammar be used, a poor-bodied, slowly-drying varnish will result. Dammar varnishes, though pale, are cloudy, owing to imperfect solution of the dammar. They are clarified by stirring into every 20 lb. of varnish 1½ lb. of absolute alcohol; the varnish, however (like every cloudy solution), darkens in the clarifying process. Dammar dissolved in benzol yields a perfectly limpid, clear solution, and thus gives a better and a quicker-drying varnish than spirits of turpentine. *Photographic Varnish.*—A good negative varnish for proofs on paper, when sufficiently thinned, is got in the cold by dissolving 8 parts of dammar in a mixture of benzol 90 parts and absolute alcohol 10 parts (all by weight). The resin is gelatinized in alcohol before adding the benzol. Lamb and Boyd make a good varnish by adding amylic alcohol to spirits of turpentine or to benzol in the ratio of 20 to 80 per cent of the total solvent according to rapidity desired in drying. For quick drying 20 per cent of amylic alcohol suffices. *Example.*—Dammar 20 lb., benzoin 20 lb., solvent 120 to 240 according as varnish is for metals, wood, or paper.

For the production of liquid bronze acid-free varnish should be used, as bronze ground with ordinary varnish will form verdigris. Two methods may be used: (1) Neutralize the dammar, pour 20 lb. of petroleum benzene over 7 lb. of finely-ground dammar, and dissolve by repeated shaking. Next add to the solution 5 lb. of a 10 per cent aqueous solution of caustic soda and shake up well for ten minutes. Two layers will form on standing, the upper one of dammar dissolved in benzene, and the lower aqueous one containing the dammar acids dissolved as soda salts. Pour off the benzene layer, agitate again energetically with another 5 lb. of the 10 per cent caustic soda solution. Now set aside for complete clarification and separation of the two liquids. The dammar solution syphoned

off will be perfectly free from acid. To obtain gold bronze varnish add to the neutralized dammar solution about 2½ lb. of bronze or brocade per gallon. (2) Or else carefully mix 10 lb. of finely-ground dammar with 3 lb. of soda ash and heat to fusion, in which state it is maintained two to three hours with frequent stirring. Now let cool, grind the turbid mass obtained, and pour 1 gallon of coal benzene or petroleum benzene over it in a flask. By repeated shaking of the flask the soluble portion of the molten mass is dissolved; filter after allowing to settle. Into the filtrate put 3 to 4 lb. of bronze powder of any desired shade, the brocades being especially well adapted for this purpose. If the metallic powder remains distributed over the mass for a long time, it is of the right consistency. If it deposits quickly, it is too thin, and a part of the solvent must be evaporated before stirring in the bronze powder.

Gold Bronze Varnish.—According to "Kraft und Licht" this varnish must be free from acid, or verdigris will form on the bronze varnished with it. It gives the following directions for making the varnish: Dissolve 5 lb. of powdered dammar in 10 lb. of petroleum ether. Then add 5 lb. of a 10 per cent solution of caustic soda, shake well for ten minutes and allow to stand. Decant the dammar solution which rises to the top from the aqueous solution of resinates below it, and treat it again with a fresh lot of lye exactly like the first in strength and quantity. Then mix the neutralized solution with the bronze. Another method is to mix 10 lb. of powdered dammar with 3 lb. of powdered calcined soda, and then fuse the mixture, keeping it fused for two or three hours with plenty of stirring. Then powder the cold mass and extract the deacidified resin with petroleum ether, and mix the filtered solution with the bronze. If no excess of the ether has been used the bronze powder will remain suspended for a long time in the solution. If it settles too rapidly some of the petroleum ether must be evaporated off.

Insecticide Varnish for Books.

Dammar	2 lb.
Mastic	2 lb.
Canada balsam	1 lb.
Creosote	½ lb.
Methylated spirit	2 gals.

Crystal Varnish.—Dissolve dammar in its own weight of turpentine and thin to the right consistency.

CHAPTER XXIV.

INDIA-RUBBER, INSULATING, MASTIC, AND MATTE SPIRIT VARNISHES.

VII. *India-rubber and Gutta-percha Spirit Varnishes* are chiefly used to render the articles or objects to which they are applied impermeable to water and to air. Many coatings are waterproof, few airproof. But if rubber varnishes are most often used with a linseed oil vehicle, yet varnishes, oil or spirit, into which rubber enters dry slowly. The best solvents are benzol and spirits of turpentine in which rubber swells and becomes transparent but does not actually dissolve. Rubber dissolved in caoutchouc oil is not often used. As a great bulk of solvent is required the percentage of solids in the varnish is small, and there is no gain in volatilizing the solvent as the thicker varnish would not dry. Rubber cut into strips and dried at 40 to 50° C. (104 to 122° F.) dissolves more freely and yields a better varnish. *Proportions:* (1) Benzol 1 gallon, rubber 1 lb.; heat on the bath till dissolved. (2) Turps ½ gallon, rubber 1 lb.; digest forty-eight hours; add another ½ gallon turps and complete solution on the water-bath. (3) *Colourless Rubber Solutions.*—The rubber is covered with twice its weight of carbon disulphide and kept in contact until it first swells and then yields a homogeneous jelly which on adding benzol dissolves completely. The carbon disulphide is distilled off on the water-bath. A more colourless solution is thus obtained than with benzol alone. (4) *Photographer's Varnish.*—Rubber 2 lb., ether[1] 1 lb.; dissolve on water-bath; used to coat funnels, small vessels of wood, papier mâché and glass. (5) *Complex Waterproof Eggshell Gloss Varnish for Wood.*—Soak 2 lb. of india-rubber cut small in 10 lb. of oil of turpentine. When it has swollen, add 10 lb. more of turpentine and dissolve the rubber with gentle heat. Mix the solution in 22 lb. of boiled oil and 11 lb. of rosinate of manganese and heat to 120° C. till clear. Then allow to cool to 80° C., and add to the mass seven times its bulk of a 40 to 50 per cent solution of shellac in spirit, and one-third of its bulk of a mixture of copaiba balsam, with five times its weight of boiled oil. The varnish is applied with a pad or a soft brush. The coats resist water, vinegar, wine, beer, and all ordinary liquids. (6) Dissolve 50 lb. dammar and 25 lb. of rubber in 6 gallons

[1] The formula prescribes that the ether should first be reduced by shaking with water to one-fifth of its original volume.

turps, and when dissolved add 6 gallons of boiled oil and filter. (7) *Varnish for Fret Work.*—Dissolve 12 lb. of rubber in a mixture of 25 lb. turps and 12 lb. rectified naphtha; mix with 6 lb. warm copal varnish. The proportions may be varied to 1 lb. rubber, 6 lb. turps, 1 lb. naphtha, and 6 lb. copal varnish. (8) *Varnish for Morocco.*—Rubber 6 lb., turps 6 gallons; digest for a few days; when the turps has been absorbed, again add an equal amount and digest on the water-bath till homogeneous; then add to 8 gallons of copal varnish made in proportion of pale copal 1 lb., boiled oil ¾ lb. Mixing is done at a moderate heat until the rubber solution is well incorporated in the varnish. (9) *Varnish for Rubber Goods.*—Vulcanized rubber 5 lb., ordinary rubber 20 lb., turps 15 gallons.

Elastic and Durable India-rubber Spirit Varnishes.—The layer of resin left by the evaporation of a spirit varnish may answer the requirement of brilliancy, but is usually brittle and of small lasting power. The reason of these defects is the impossibility of adding drying oils to the varnish. Even the usual additions of turps, elemi, and other semi-liquid resins remedies the trouble only imperfectly, and at the cost of introducing fresh difficulties. Although, however, drying oils will not mix with spirit varnishes, the fatty acids which they contain will do so, and give to the spirit varnish the elasticity and durability of an oil varnish, and they dry by oxidation quite as well as the oils themselves. This property also permits the addition of india-rubber to spirit varnish, a thing hitherto impossible. The boiling fatty acids dissolve india-rubber easily, and the solution can then be added to the spirit varnish without any precipitation of india-rubber taking place. The addition of the fatty acids to a spirit varnish also lessens the too rapid drying of it, and enables large surfaces to be coated uniformly and without showing brush marks. The following is a recipe for one of these varnishes: Dissolve 200 lb. shellac and 200 lb. of soft Manila copal in 250 lb. of 96 per cent spirit mixed with 200 lb. of heavy petroleum spirit. When cold add 75 lb. of fatty acid of linseed oil, 75 lb. of fatty acid of wood oil, 25 lb. of india-rubber, and 2 lb. of manganese borate. The two last should be dissolved in the fatty acid before the latter is added to the solution of the resins.

Cements for Rubber and Gutta-percha.—Cements for the above materials, useful both in the workshop and in the house, can be prepared as follows: (1) To fasten leather on gutta-percha, a hot mixture of gutta-percha 50 parts, asphalt or pitch 100 parts, and turpentine oil 15 parts, is used. (2) For two surfaces of leather, e.g. boot soles, an elastic gutta-percha cement that will neither tear nor break when bent is employed. It is made by dissolving 10 parts of gutta-percha in 100 parts of benzol, pouring this solution into 100 parts of linseed varnish, and shaking the whole up together. (3) To attach rubber to metal, use can be made of a 10 per cent solution of shellac in ammonia. After standing for three or four weeks the preparation can be used cold; it is water

and gas tight, and will also fasten hard rubber. (4) Cement for leather-driving belts is prepared by kneading together a mixture of 10 parts of carbon disulphide and 1 part of turpentine oil, and enough gutta-percha to make a stiff paste. The leather must be freed from grease, and roughened, and the parts pressed together until the cement has dried. (5) A cement for repairing rubber shoes is made from a 4 per cent solution of caoutchouc in chloroform, and a solution of 10 parts of caoutchouc and 4 parts of rosin in 40 parts of turpentine oil, the two being mixed in equal proportions before use. (6) The following solutions are useful for cementing caoutchouc: 100 parts finely shredded caoutchouc, 15 parts resin, and 10 parts of shellac, dissolved in carbon disulphide; or 1 part of caoutchouc, 7 parts gum mastic, and 50 parts chloroform left to dissolve at leisure.

	Parts by Weight.
India-rubber	10
Chloroform	6
Mastic	2

This size is also good for making glass adhere to other hard surfaces.

Waterproof Cement for Leather, Caoutchouc and Balata.—A waterproof cement for leather, caoutchouc, or balata is prepared by dissolving gutta-percha, caoutchouc, benzoin, gum lac, mastic, etc., in some convenient solvent like carbon disulphide, chloroform, ether, or alcohol. The best solvent, however, in the case of gutta-percha is carbon disulphide, and ether for mastic. The most favourable proportions are as follows: Gutta-percha, 200 to 300 parts to 100 parts of the solvent, and 75 to 85 parts of mastic to 100 parts of ether. From 5 to 8 parts of the former solution are mixed with 1 part of the latter, and the mixture is then boiled on the water-bath, or in a vessel fitted with a water jacket.

Imitation Gutta-percha.—A new method of making this substance has been introduced by Siemens and Halske, of Berlin. The ingredients consist of caoutchouc and a rosin soap, the latter compounded, for example, of 100 parts of rosin, 100 parts of Carnauba or Ocuba wax, and 40 parts of gas tar, melted together and passed through a sieve. They are then heated to about 170° to 180° C., and slowly saponified by stirring with 75 parts of milk of lime of specific gravity 1·06. The product is next put into a kneading machine along with an equal quantity of caoutchouc cuttings, and worked on this machine at a temperature of 90° C. or over. When sufficiently kneaded, the mass can be rolled to render it more uniform.

Insulating Varnishes.—Efforts have been made of recent years to cheapen the passage of electricity so as to cope with modern progress in electro-technics. Conductors require to be perfectly insulated to prevent current leakage, and men and animals come in contact with bare conductors with serious, if not fatal results. A

portion of the first samples of gutta-percha brought to Great Britain by Montgomery were handed to William Siemens who in turn sent them to his brother Werner in Berlin, and in gutta-percha Werner Siemens discovered the first good insulator. He also designed a machine for coating wires with it. Gutta-percha is the insulating material *par excellence* for submarine cables, and laid at the bottom of the sea gutta-percha maintains its insulating powers unimpaired for ages. As an underground insulator it succeeds well in damp earth. But exposed to the air it oxidizes, hardens and cracks, and the insulation is destroyed or defective. Numerous attempts have been made to prevent the oxidation and resulting crumbling of gutta-percha exposed to the air. To protect museum specimens of gutta-percha from disintegration by air they are covered with a coat of varnish. Naturally in trying to improve on gutta-percha or to find a substitute for it, it was tried to cheapen it, but it still retains its supremacy as the insulator *par excellence* of submarine cables. But rodents and other animals attack it in underground conduits, and paper coated with rosin oil, or some such-like composition, has been for some years successfully used as an insulator on land, especially for high-tension current. In submarine telegraphy the current is always a low-tension one. The necessity for some liquid for impregnating and supplementing the insulation on electrical apparatus has long been recognized. It is not sufficient to have a varnish that merely forms a more or less waterproof covering outside the coils. A substance is required that will reach right down to the deepest layer. The need of the extra insulation is difficult to explain. Coils have been wound and machinery has been run with simply the silk or cotton covering over the copper wire, and though this has initially appeared sufficient the original insulation has, in time, given out. The insulation varnish, therefore, is not so much needed as an insulator, but to maintain the initial insulation resistance over a longer period more constant.

Linseed oil is debarred owing to its oxidation to a brittle substance; moreover, it may be so applied that it acts as a carrier of oxygen to paper and burns it so that in a few years the paper is as brittle as if it had been charred. This occurs when it has been saturated with linseed oil dissolved in its own volume of spirits of turpentine. If a diluent be required then a neutral petroleum spirit should be used. Paraffin wax has been extolled as the insulator from all points of view, especially an article sold under a trade name said to be made by dissolving paraffin wax in petroleum naphtha and raising the melting-point by a special process to 300° C. (? how). But paraffin has the defect of sweating out from any coating in which it is an ingredient. Moreover, it is almost as brittle as a thin film of ice when cold.

Few varnishes are effective insulators. Such varnishes must leave a permanent waterproof film and so far elastic as to allow of expansion by heat and contraction by cold of the organ of the

apparatus on which it is applied. It must not peel, crack, or blister with heat, age, or vibration, and it must not act chemically on the cotton, silk, or paper, or other insulation material, or on the copper itself. Permanence is the chief requisite. Shellac varnish, one of the first insulators to be used, is still often used in spite of many defects for small repairs by unskilful hands. The film softens at a moderate heat. It is urged that being formed by dissolving shellac in methylated spirit that as methylated spirit contains water that the varnish is more or less hygroscopic. It is also urged that it rapidly powders under the vibration of the machinery. But shellac itself is fairly elastic when pure, yet as the varnish is often adulterated with Manila copal and rosin such complaints are better founded in regard to the sophisticated article than the pure article. But commercial shellac of commerce, it is urged, nearly always contains free acid. Be that as it may, the alcohol in which it is dissolved invariably does so. This free acid attacks the copper and can be recognized on a coil insulated by this means by the green discoloration it produces. Shellac is, therefore, it is urged, unsuitable for most electrical purposes for which an insulating varnish is required. Most defects of shellac varnish also occur in copal and asphaltum varnishes. Under vibration and heat they rapidly powder, become entirely useless; besides, nearly all varnish resins contain free acid. Attempts to remove brittleness by slow-drying oils improved matters at the outset, yet the film finally became as brittle as ever.

Coils are dried before varnishing in a vacuum oven at a temperature of 100° C., and the hot coil put into a bath of the varnish and left until thoroughly impregnated, after which it is removed and replaced in the baking oven for a few hours, suitable provision being made to allow the coil to drain, after which it is cooled. Some vacuum ovens permit of dipping and drying without removal from the oven, which, of course, ensures a more thorough job than when the coil is exposed to the air, even, it may be, at a high temperature.

To test varnishes apply them to linen or paper with a brush, in two directions at right angles to one another; or the linen may be dipped in the varnish, the top and bottom of the piece being exchanged at each successive dipping to ensure as even a coating as practicable. It is important to use the same thickness and quality of linen in all tests. Batiste linen is a good standard. The sample is then dried generally at the temperature recommended by the manufacturer, until it is no longer sticky. The disruptive strength of these samples is then tested, cold and warm, flat, and after creasing, and the average and minimum values for several samples are recorded. The samples are also tested as to freedom from acid. The drying properties of the insulating varnish should also be determined both in the air and in the stove, after which the power to stand high temperatures should be determined, by superheating until the varnish either runs or chars.

To test effect of varnish on copper wires mix copper turnings

with the varnish. They will turn green if the varnish acts on them in any way. To test if watertight apply the varnish to a piece of cotton duck; moisten the back uncoated part with the saliva, place against mouth and blow. If no bubbles show it is airtight, and if airtight it is in all probability also watertight. But make a bag, coat it with the varnish, place a sufficiency of dehydrated blue vitriol or dehydrated green vitriol in the bag, immerse in water, and if it be not watertight these reagents will be turned blue or green as the case may be.

Some Recipes for Insulating Varnishes.—The following recipes are not free from the defects just discussed, but they are quoted from an authority who gives them as "the best known":—

1. Melt together 20 lb. of asphaltum and 4 lb. of sulphur. Then add 50 lb. of drying oil or cotton-seed oil, keeping for five to six hours at 160° C. Finally dilute with oil of turpentine.

2. Keep 30 lb. of elaterite, with 20 lb. of drying oil, for five to six hours at 200° C. Then add 30 lb. of fused asphaltum and maintain the temperature for another three to four hours. Then add 10 lb. of drying oil and dilute with oil of turpentine.

The following two recipes will give products very suitable for use where the currents are only of low tension:—

TABLE CXII.—SHOWING RECIPES FOR VARNISHES FOR LOW-TENSION CURRENTS.

	I. lb.	II. lb.
Shellac	4	4
Sandarach	2	4
Elemi	—	1
Linoleic acid	2	—
Alcohol	15	20

Insulating Material.—*Stearine Pitch* has been recommended as an insulating agent, owing to its impermeability, elasticity, low electrical conductivity, and lack of smell. According to Dupré and Icard, it may be applied for insulation purposes either in solution in carbon disulphide, etc., or direct, in which latter event it is either melted or else softened by contact with a hot iron. For the same purpose it may be incorporated with other substances that either assist or counteract its own properties, such as tar, various resins, carbonate of magnesia, talc, graphite, asbestos. But stearine pitch has many serious defects from an insulation point of view, and these may readily be gathered from Vol. II of this treatise, pp. 37, 38.

For information in regard to numerous substitutes for gutta-percha and insulating compositions (Chatterton's compound, etc.), see "India-rubber and Gutta-percha," 2nd edition, pp. 492, 493 (Scott, Greenwood & Son), also "Mineral Waxes," published by the same firm.

TABLE CXIII.—ELECTRIC INSULATING COPAL SPIRIT VARNISH.

Clear Manila gum	18	parts	wt.
Neut. K. rosin	18	,,	wt.
Columbian spirits[1]	32	,,	fld.
74° B. petroleum naphtha	16	,,	fld.

Use steam warm. Keep covered.

VIII. *Mastic Varnishes* are highly esteemed for oil paintings, water-colour pictures, cardboard, paper, etc., but high price makes its use expensive. (1) *Solution in Alcohol.*—It yields a quick-drying varnish. Water-colour and paper varnishes are made as follows :—

TABLE CXIV.

	Water-colour.	Paper.	Bookbinder.
Mastic (lb.)	5	4	3
Alcohol (lb.)	14	14	20
Venetian turpentine (lb.)	2	$2\frac{1}{2}$	—
Bleached shellac (lb.)	—	—	1

As alcohol only dissolves 90 per cent of mastic, the residue is employed in making mastic varnishes with spirits of turpentine as the solvent. But complete solution is got in alcohol by addition of a little spirits of turpentine. (2) *Spirits of Turpentine Solution* is highly esteemed for pictures (mixed with linseed oil it yields artists' *megilp*). One lb. of mastic is dissolved in $1\frac{1}{2}$ lb. of spirits of turpentine, either on the cold or on a water-bath. Acetone has been recommended as a solvent, mastic being very soluble in the cold in that reagent.

TABLE CXV.—MIXED MASTIC SPIRIT VARNISHES.

	I.	II.	III.
Shellac	50 lb.	—	—
Mastic	27 ,,	90 lb.	30 lb.
Sandarach	—	45 ,,	120 ,,
Venetian turpentine	—	45 ,,	45 ,,
Methylated spirit	27 gals.	60 gals.	60 gals.

TABLE CXVI.—MASTIC SPIRIT VARNISHES.

	A.	B.	C.	D	E.	F.
Mastic (lb.)	6	7	6	30	30	10
Camphor (oz.)	—	—	3	—	—	—
Rosin W.W. (lb.)	—	—	—	20	20	35
Dammar (lb.)	—	—	—	30	20	20
Turps (gal.)	1	1	1	10	10	10

A Finest, B Finest Strong, C Finest Camphorated, D Fine, E Mastic, F Common.

Cerulline—A Spirit Varnish Enamel.—Cerulli prepares a paint for application to plaster, cement, stone, or any hard substance without using oil or oil-varnish as a component material.

[1] Pure methyl alcohol.

For enamel paint destined to exhibit a bright surface, a solution of mastic is prepared by dissolving 355 grammes of mastic in the drop form, and 50 grammes of lavender oil in 1 litre of turpentine, the whole being heated at 100° C. (212° F.) on the water-bath, and filtered in a lukewarm condition.

On the other hand, 365 grammes of powdered pigment are thoroughly mixed by milling with 200 grammes of weak caoutchouc mordant, the resulting paste being set aside in a closed receptacle for twenty-four hours. It is then liquefied and made ready for use by the addition of some of the mastic solution, care being taken to have the whole very thin, as it tends to thicken afterwards. If desired to be very hard, it may be thinned down with lavender oil, or, preferably, with turpentine slightly acidified by the addition of four drops of nitric acid per litre.

For dull-surface paints the same ingredients are supplemented by a solution of 20 parts of virgin wax in 100 parts of ordinary petroleum, prepared over the water-bath.

The subjoined formulæ show the proportions more exactly :—

TABLE CXVII.—CERULLINE SPIRIT VARNISH ENAMEL.

A.

MASTIC SOLUTION.

Turpentine	832 grms.
Gum mastic	355 ,,
Lavender oil	50 ,,

Heat on the water-bath at 100° C. for six hours.

B.

PETROLEUM SPIRIT SOLUTION.

Petroleum spirit	800 grms.
Virgin wax	80 ,,
Lavender oil	50 ,,

heated together on the water-bath for three hours.

C.

LUSTROUS ENAMEL PAINT.

Powdered pigment	365 grms.
Weak mordant	200 ,,
Mastic solution	400 ,,
Acidified essential oil	35 ,,

mixed, and left at rest for twenty-four hours.

D.

MATT ENAMEL PAINT.

Powdered pigment	365 grms.
Weak mordant	200 ,,
Mastic solution	200 ,,
Wax-petroleum solution	235 ,,

These paints are very slow in drying, and if desired to dry quickly, must be mixed with a little siccative oil.

IX. *Matt Varnishes.*—This class of varnishes finds an extensive use in many industries, a comparatively recent application being the dipping of electric light lamps in a spirit matt varnish, so as, in a measure, to deaden somewhat the glare of the electric light. For this purpose they may be either colourless or coloured. If desired coloured, any of the numerous colouring principles soluble in spirit may be used. But, independent of this perhaps limited and rather exceptional use, spirit matt varnishes find a wide application in all numerous instances where it is desired to impart a dull lustre to polished or varnished surfaces. The matt varnish in question must be of such a composition and of such a nature as not to remove or alter in any way the polished surface or coating of varnish on which it may be applied. Both spirit varnishes and water varnishes are used for this class of work. In the selection of colours, care must be taken to use only those which do not dry with a fluorescent surface. Moreover, the coating must not be granular or powdery, so as to give rise to a whitish, unpleasant appearance. Water-matt varnishes are made by dissolving shellac in borax, soda, ammonia, or potash, heat being applied until solution is effected. The liquid is then filtered, diluted with water, and coloured with a suitable colouring principle, such as Cassel brown, lampblack, etc.

Reh's Matt Varnishes.—Reh makes a matt varnish, the manufacture of which is rather complicated and involved. First of all, he makes three mixtures as follows:—

I. (*a*) 60 parts of turpentine; (*b*) 6 parts sugar of lead; (*c*) 20 parts of absolute alcohol. *b* and *c* dissolve with the aid of heat, and add to *a*.

II. 3 parts of camphor and $1\frac{1}{2}$ parts of spermaceti. Mix together by melting.

III. 1 part of Manila copal, 2 parts of methylated spirit. Dissolve in the cold, and filter.

TABLE CXVIII.—FINISHED MATT VARNISH.

	Parts by Weight.
Mixture I.	12
Spirits of turpentine	6
Mixture II.	6

This gives a turbid solution, which is clarified by vigorous agitation with methylated spirit 36 parts, after which add mixture III. 30 parts. This varnish may be applied either with a brush or with a wad.

Reh's Black Matt Varnish.—It may be coloured black as follows:—

	Parts by Weight.
Matt varnish	600
Nigrosine solution	9
Methyl violet solution	1

Gawalowsky makes his matt varnish as follows :—

	Parts by Weight.
Seed lac	120 to 140
Ammonia	90 „ 110

diluted with

Water	800
Logwood extract (solution of)	12
Sulphate of copper	0·1
Sugar of lead	0·1

Enough lampblack is added to yield a deep black.

Matt Varnish for Metals.—A very dilute solution of shellac in methylated spirit coloured by a dilute solution of red or yellow grass-tree gum in the same solvent.

Another formula is :—

	Parts by Weight.
Methylated spirit	29
Spirits of turpentine	6
Sandarach	6½
Venice turpentine	16

Coloured with vegetable colouring principles, which always give the best results. The "bloom" of aniline dyes debars them.

The following are the compositions of a few spirit matt varnishes :—

	lb. oz.
Sandarach	— 9
Mastic	— 2
Ether	6 0
Benzol	1½ to 4½ lb.

In another formula the ingredients are :—

	lb.
Sandarach	1
Ether	10
Toluol	3 to 5

Again, a spirit varnish used for this purpose in Switzerland would appear to be a sort of highly dilute patent knotting, viz. :—

Alcoholic solution of shellac	1 lb.
Methylated spirit	2 gals.

Matt Varnishes.—In the preparation of matt spirit varnishes use may be made of mixtures of acaroid resin solutions with Manila copal dissolved in spirit; and additions of fine starch, gypsum, fullers' earth, and other loading ingredients are also used to produce a matt effect. There being no black or dark resin that is soluble in spirit, it is necessary to darken spirit varnishes with lampblack, no more being used than is necessary to impart the desired depth of colour. Spirit varnishes can also be made to dry matt by admixtures of solutions of celluloid or collodion wool and benzol or turps; but the former, in admixture with water and ammonia, which re-dissolves the precipitated resin, mostly dries so irregularly and stripy that it is generally unsuitable for large surfaces. A volatile colourless matt varnish may be prepared by mix-

ing about 25 per cent of French or American turps with 75 per cent of 95 per cent spirit, any tendency to separate on standing being counteracted by the addition of small quantities of one or other ingredient, until the resulting liquid is perfectly clear. This product is then used for dissolving 15 to 20 per cent of sandarach and 3 to 5 per cent of larch turpentine, and filtered, the varnish being coloured if desired. Another formula consists in dissolving 5 parts of Manila copal and 5 of red acaroid resin in 20 parts of spirit. According to a third recipe, 18 parts of sandarach and 4 of mastic are dissolved in 192 parts of ether, and treated with an addition of 40 to 144 parts of benzol. Still another recipe is composed of 25 parts of garnet shellac, 5 of larch turpentine, 100 parts of spirit, and 10 parts of boric acid.

Visiting-card Matt Varnish.—Bleached shellac 100, glycerine 20, galipot 20, methylated spirit 200, ethyl ether 100.

Matt Varnish for Photographer's Work.—Four lb. dammar are dissolved in 30 lb. toluene by heating to 40° C. and the solution mixed with constant shaking with an ethereal solution of sandarach (10 lb. to 30 lb.); finally a very little absolute alcohol is added.

Hugue's Completely Colourless Matt Varnish consists of 40 oz. of sandarach dissolved in 500 oz. (wt.) of ether, and 10 oz. of Canada balsam added.

Photographic Matt Varnish.—Sixty lb. of sandarach and 1 of Venice turpentine are dissolved in 50 lb. of ether, and when solution is complete 20 lb. of benzol are run in as a thin stream with constant stirring. A sample is spread on glass, and put away out of contact with dust for about ten to fifteen minutes. If dry and shiny at the end of that time, the mixture needs more benzol, but not more than 24 parts of this latter should be used in all, as otherwise the varnish would be cloudy, and the surface too rough. The varnish is very fluid, but covers perfectly, and is harder than any other of the kind.

Varnish for Doll-makers.—(1) Five parts of white wax are dissolved in 25 of ether, and then mixed with 100 parts of collodion and 1-20th part of oil of rosemary. (2) Two parts of French resin and 6 of pale Manila copal are dissolved in 52 of ether, and well mixed with 32 parts of collodion.

Picture-frame Varnishes.—Dull varnishes for picture frames may be prepared from the following stock solutions: No. I.: Palest Manila copal 60 parts, thick turpentine 10, in 85 parts of spirit. No. II.: Sandarach 60 parts, thick turpentine 10, in 85 parts of spirit. No. III.: Acaroid resin (pp. 235-7) 70 parts, in 75 parts of spirit. Varnish No. I. consists of 2 parts of solution I., 1 part of No. II., and 2 parts of No. III. Varnish No. II. is a mixture of equal parts of solutions Nos. II. and III. Both may be converted into black varnishes by incorporating with them 2 to 3 per cent of nigrosine. Acaroid resin has not made much headway in varnish-making, for one reason, because of its dark colour, and because it does not mix

well with Manila copal. In times, however, when shellac is very dear, as often occurs, acaroid resin forms a very useful adjunct, being cheaper and much harder than Manila copal, besides mixing with resin and sandarach. Although when newly applied to glass these mixed varnishes are cloudy, this defect vanishes in the course of a few weeks.

Some Additional Recipes for Matt Varnishes.—Dissolve caoutchouc or unvulcanized india-rubber in mineral naphtha, and then add sufficient asphaltum to make the compound of a suitable consistence. To get the asphalt to dissolve, stand the vessel in another vessel containing boiling water so as to effect solution at a moderate heat. This is necessary so as to avoid vapourizing the spirit, which would then ignite if near a naked flame. A flexible, dull varnish for metals, leather, wood (non-porous), and other materials is prepared by dissolving black india-rubber in oil of turpentine, and then mixing in sufficient lampblack to make the compound of a suitable consistence to dry without a gloss. Another dull varnish for metals is prepared by rubbing up good lampblack with oil of turpentine, and then mixing this with a little copal varnish—just sufficient to cause the varnish to attach itself to the metal, but not sufficient to enable it to dry with a gloss. The following varnishes are suitable for wood, metal, paper, and non-porous materials. A coat of size should be first laid on: No. 1: 2 parts mastic in "tears" (i.e. not ground), 8 parts sandarach (ditto), 96 parts methylated spirit, 31 parts benzol, lampblack *q.s.* Dissolve the resins in the mixed spirit, and then grind up the lampblack in the varnish thus prepared, using sufficient to dry without a gloss. No. 2: 9 parts sandarach resin, 2 parts mastic, 100 parts sulphuric ether, 40 to 50 parts benzol, lampblack *q.s.* Prepare as in No. 1. Colour methylated spirit with aniline black, and then dissolve therein a few per cents of benzoin and 1 per cent of boracic acid. [All parts by weight.]

TABLE CXVIIIA.—WATERPROOF VARNISH FOR BEACH SHOES.

	A	B	C
Water in gals.	15	15	15
Borax in lb.	5	5	5
Glycerin in lb.	3	2	2
Liquor ammoniac 0·880	1	1	0·25
Shellac in lb.	25	22	25
Dye yellow in lb.	1	0	8
Dye brown in lb.	—	0·3	—
Dye orange in lb.	—	1·0	0·3

A = Yellow; B = Brown; C = Pale Brown. For A and C use Bleached Shellac and for B Garnet.

CHAPTER XXV.

ROSIN SPIRIT VARNISHES—SANDARACH SPIRIT VARNISHES—SHELLAC WATER VARNISHES—SHELLAC SPIRIT VARNISHES—SPIRIT VARNISH ENAMELS—SUNDRY SPIRIT VARNISHES.

X. *Rosin Spirit Varnishes.*—Methylated spirit if of full strength is a good and cheap solvent for rosin, far better than spirits of turpentine, it is, in fact, a great mistake to use either spirits of turpentine or any variety of turpentine oleo-resin in a varnish in which rosin is the only solid. Both the essential oil and the oleo-resin accentuate in the worst possible manner the tackiness of rosin. Most text-books are very misleading in this respect; as a rule, they say rosin varnishes, cheap but not durable, are improved by a little Venice turpentine, sandarach, or mastic. The two latter may improve solutions of rosin in methylated spirit in regard to brittleness, but Venice turpentine if it improves the brittleness slightly accentuates the tackiness. By far the best solvent for rosin is clean, well-rectified petroleum naphtha or coal-tar naphtha, especially the variety of coal-tar naphtha known as solvent naphtha, and the best addition is fused linoleate of lead dissolved in naphtha. Should the maker, however, have a predilection for the addition of solid turpentine in the form of an oleo-resin, then let him use Burgundy pitch and not Venice turpentine, which is a very viscous, tacky substance and slow to dry, and that notwithstanding that some authors do not consider a varnish formula complete without it. Rosin solvents take from one to one and a half times their own weight of rosin to make a decent varnish. Ten lb. of rosin to the gallon of turps, methylated spirit, or naphtha is quite thin enough for many purposes. Just as naphtha is the best solvent for rosin, so also is a naphtha solution of dammar one of the best additions than can be made to a naphtha rosin varnish, say 10 per cent of dammar in its own weight of naphtha on the weight of the rosin, or the proportions might be varied thus, when a methylated spirit solution of rosin is used:—

TABLE CXIX.—ROSIN SPIRIT VARNISHES.

	A.	B.
Rosin	90 lb.	90 lb.
Sandarach	—	10 ,,
Dammar	10 lb.	—
Methylated spirits	—	10 gals.
Naphtha	10 gals.	—

Attacking both resins conjointly with the solvent, labour is saved. Sandarach or shellac is the best addition to methylated spirit solutions of rosin, but then the vendor, or rather the maker, does not sell them as rosin varnishes, but as shellac or sandarach varnishes respectively. Solutions of rosin in naphtha pure and simple are used as vehicles to coat iron drums, kegs, and it is said even ships' bottoms, mixing with lampblack for black, Venetian red and red lead mixed for red, Brunswick green for green, and so on. Such varnishes would be greatly improved by an addition of pure well-boiled linseed oil. A varnish for toys and common articles is made by simply dissolving French or American rosin in methylated spirits. The process is similar to that given for shellac varnish. The colour varies with that of the resin used. Generally Venetian turpentine is added.

The general formula is :—

Rosin	20 parts.
Alcohol, 95 per cent	12·7 to 14·5 parts (wt.).

There may be added :—

Venice turpentine	8·6 parts (wt.).

If spirits of turpentine be the solvent used, as rosin is very soluble therein, the operation may be done in the cold, but heat acclerates solution.

If with a view of improving the varnish Venice turpentine, sandarach, or mastic be added to the resin, they are all cautiously melted together, and when the mixture is homogeneous the spirits of turpentine is added after withdrawing the vessel from the fire.

The usual formula is :—

Rosin	20 parts (wt.).
Spirits of turpentine	12 " "
Venice turpentine / Sandarach or mastic	6 to 40 " "

But it is then necessary to increase the proportion of spirits of turpentine, allowing 3 to 6 parts of spirits for each part of substance other than resin.

Sometimes rosin varnish made with turpentine if kept in a rather warm place turns turbid. It may be clarified by heating and adding 5 per cent of spirits of turpentine.

Driers with a Rosin Base.—Filsinger has proposed to replace oil driers by a mixture which approaches them very closely in their result. The principal ingredient is a rosin soap, prepared as follows : In a copper pan 50 lb. of caustic soda are dissolved in 15 lb. of water, and brought to the boil, then 100 lb. of finely ground rosin are added, with constant stirring, and the liquid heated until limpid. The whole is allowed to cool, and the solution decanted from the resin soap in the bottom. This soap is dissolved in a small quantity of water, to which has been added a little sal ammoniac. The pigments are ground with this mixture. A paint is thus obtained which

dries quickly, and which will take a coat of varnish, but if the process is economical and the appearance pleasant, the durability on the other hand is but very poor and the rationale of the process is very crude.

Rosin Water Varnish.—Rosin 8 lb., soda crystals 3 lb., water 2 gallons; boil until all the rosin is dissolved (formation of sodium rosinate). The soda crystals should be free from Glauber's salts.

XI. *Sandarach Spirit Varnishes.*—This white hard spirit varnish is used for labels, placards, papier mâché work, turned articles, cardboard, leather, wood, and metals. Methylated spirit is *the* solvent for sandarach, but sometimes spirits of turpentine is used in conjunction with the former. The varnish is straw-yellow to deep yellow according to the colour of the sandarach, with a beautiful lustre in thin coats. Venice turpentine, Burgundy pitch, etc., are added, to give elasticity. (1) Livache gives the general formula as sandarach 5 lb., Venice turpentine 3 to 5 lb., alcohol 95 per cent 15 to 24 lb. (2) In varnishes used to fix drawings and water-colours, etc., expected to give a thin coat, the alcohol may run to 45 lb. (3) For use on wood the 5 lb. of Venice turpentine may be replaced by 2 lb. of elemi or mastic; or (4) by adding 5 lb. of a solution of equal parts of rosin and shellac dissolved in 95 per cent alcohol. (5) On metals a mixture of mastic, shellac, and benzoin; or (6) a mixture of mastic and Venice turpentine may replace the mastic, and instead of alcohol a mixture of equal parts of alcohol and spirits of turpentine is used. (7) A *flexible* varnish is made by melting 4 lb. of sandarach and 2 lb. of rosin and dissolving in 1 gallon of spirits of turpentine and adding a solution of rubber in coal-tar naphtha. (8) A *negative* varnish: dissolve 1½ lb. of sandarach in a gallon of methylated spirit. To prevent dullness in drying add 1½ oz. of spirits of lavender. (9) Valenta's negative varnish: dissolve on the water-bath 10 lb. of sandarach in 4 gallons of benzol, 4 gallons of acetone, and 2 gallons of absolute alcohol. The materials are heated together on the water-bath.

TABLE CXX.—WHITE SPIRIT (SANDARACH) VARNISHES FOR WOOD.[1]

	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.	L.	M.
Sandarach	36	3	25	5	12	20	3	36	3	50	8	15	3
Bleached amber	—	—	—	—	—	—	—	—	3	12	—	—	—
Mastic	25	3	—	5	6	5	—	36	1	36	—	—	1
Copal	—	—	—	—	6	—	—	12	—	{12, 25}	—	5	—
Venice turpentine	50	3	12	—	5	10	3	—	1	{25, 36}	1	—	½
Spirits of lavender	—	—	—	—	—	—	—	36	—	—	—	—	—
Methylated spirit	300	4g	100	60	66	80	16	400	12	400	15	80	16
Ether	—	—	—	10	—	—	—	—	—	—	—	—	—
Spirits of turpentine	—	—	—	—	—	—	—	—	—	—	1	—	—
Ground glass	—	4	—	10	8	10	—	—	2	—	—	—	2
Elemi	—	—	—	—	—	—	—	—	—	—	—	5	—

[1] All ingredients in lb. except g = gals.

A, "colourless" varnish. B, similar to A, but not so durable. C, similar to A and B (sometimes perfumed by adding benzoin); does not dry well but is rather durable. D, for same purpose. E, ditto. F, bright varnish for wood subject to friction, chairs, fans, etc. G, the Venice turpentine is melted in a well-glazed pot and the pulverized sandarach added with constant stirring. The melt is poured into cold water and the solid product crushed and dried at a gentle heat, again ground and dissolved. Dries with brilliant lustre but slowly. H, made like G; the copal, slightly moistened with a few drops of lavender, is gently fused in a glazed pot and run on to a cold marble slab, then ground. This powder is mixed with the sandarach and mastic and dissolved on the water-bath. The lavender is added after solution. The copal may be increased to the benefit of the varnish. I, made similar to H. The Venice turpentine is added after the remainder is dissolved in alcohol. J, a mixed varnish, rivalling good copal varnish. The resins are crushed (the copal moistened with alcohol), mixed, and used very dry; they are put into a matrass and the alcohol run on to them. After solution on the sand-bath the Venice turpentine is added and the whole filtered. K, for same purpose as J, dries less rapidly. L, flexible for thin wooden objects. M, furniture varnish.

TABLE CXXI.—MIXED SANDARACH SPIRIT VARNISHES (FOR COPPER-PLATE ENGRAVINGS).

	I. lb.	II. lb.
Sandarach	12	16
Mastic	4	16
Copaiba balsam	2	—
Elemi	—	30
Venetian turpentine	3	4
Methylated spirit (gals.)	5	8

TABLE CXXII.—MIXED SANDARACH SPIRIT VARNISHES (FOR OIL PAINTINGS).

	I.	II.
Sandarach	15 lb.	24 lb.
Mastic	5 "	4 "
Copaiba balsam	2 "	—
Spike oil	—	1½ gals.
Absolute alcohol	—	2¼ "
Methylated spirit	6 gals.	6 "
Venice turpentine	3 lb.	—
Turps	5 gals.	—

Russian Leather Varnish.—20 lb. sandarach; 10 lb. mastic; 2 lb. Venice turpentine; 1 lb. elemi; 1 lb. castor oil; 2 lb. birch-tar oil; 1 lb. fuchsin or ponceau for red; 8 lb. nigrosine for black; methylated spirit 20 gals.

TABLE CXXIII.—SANDARACH VARNISHES FOR VARIOUS PURPOSES.

1. Paper Varnish.

Australian sandarach	50 lb.
Venice turpentine	30 „
Methylated spirit	18 gals.

2. Paper Varnish, Second Quality.

Australian sandarach	50 lb.
Burgundy pitch	30 „
Methylated spirit	18 gals.

3. Sculptors' Varnish.

Australian sandarach	40 lb.
Venice turpentine	30 „
Methylated spirit	20 gals.

4. Pale Bookbinders' Varnish.

Australian sandarach	50 lb.
Venice turpentine	35 „
Methylated spirit	21 gals.

5. Varnish for Black and White Drawings.

Australian sandarach	20 lb.
Venice turpentine	20 „
Methylated spirit	22 gals.

6. Water-Colour Varnish.

Sandarach	40 lb.
Venetian turpentine	40 „
Methylated spirit	17 gals.

7. Varnish for Silver.

Sandarach	40 lb.
Venice turpentine	80 „
Methylated spirit	23 gals.

TABLE CXXIV.—MIXED SANDARACH VARNISHES FOR VARIOUS PURPOSES.

1.	Sandarach	60 lb.
	Mastic	60 „
	Venice turpentine	30 „
	Methylated spirit	29 gals.
2.	Sandarach	30 lb.
	Rosin	20 „
	Burgundy pitch	10 „
	Methylated spirit	12 gals.
3.	Sandarach	30 lb.
	Mastic	20 „
	Rosin	20 „
	Venice turpentine	10 „
	Methylated spirit	18 gals.
4.	Sandarach	30 lb.
	Rosin	20 „
	Elemi	10 „
	Methylated spirit	12 gals.

TABLE CXXV.—SOUNDING-BOARD VARNISH.

Sandarach	100 lb.
Mastic	12 „
Copaiba balsam	10 to 12 lb.
Castor oil	1 to $1\frac{1}{2}$ „
Methylated spirit	60 gals.

TABLE CXXVI.—SANDARACH WHITE HARD SPIRIT VARNISHES.

A. Cheap Sandarach White Hard Varnish.

Sandarach	32 lb.
Pale rosin	48 „
Methylated spirit, 64 O.P.	8 gals.

B. Sandarach White Hard Spirit Varnish.

San arach	35 lb.
Pale rosin	35 „
Methylated spirit, 64 O.P.	8 gals.

C. Sandarach White Hard Spirit Varnish.

Sandarach	40 lb.
Pale rosin	25 „
Methylated spirit, 64 O.P.	8 gals.

D. Sandarach White Hard Spirit Varnish.

Sandarach	45 lb.
Pale rosin	15 „
Methylated spirit, 64 O.P.	8 gals.

E. Extra Stout Genuine Sandarach White Hard.

Sandarach	13 lb.
Methylated spirit, 64 O.P.	2 gals.

F. Best Sandarach White Hard.

Sandarach	10 lb.
Methylated spirit, 64 O.P.	2 gals.

G. Stout Genuine Sandarach White Hard.

Sandarach	12 lb.
Methylated spirit, 64 O.P.	2 gals.

The above formulæ show in a very marked manner how the amount of solids must be increased per gallon when rosin is used so as to get a varnish with sufficient body.

TABLE CXXVII.—SANDARACH WHITE HARD SPIRIT.

Sandarach	50	20	6	25	50
Venetian turpentine	7½	—	—	15	—
Elemi	—	—	—	—	—
Mastic	—	10	8	—	—
Rosin	—	10	—	—	—
Camphor	—	2	—	—	—
Thick turpentine	—	—	—	—	80
Methylated spirit	150	120	150	100	150

TABLE CXXVIII.—TRANSPARENT VARNISH.

	Parts by Weight.
Powdered sandarach	4
Venice turpentine	7
Spirits of turpentine	28

Dissolve the turpentine and the powdered gum sandarach over a water-bath in the spirits of turpentine. Before this varnish is used the bottle should be exposed to the sun for about an hour.

TABLE CXXIX.—VARNISH FOR STEEL (DRESS SWORDS, ETC.).

	Parts by Weight.
Sandarach	15
Small mastic	10
Elemi	5
Camphor	8

Dissolve the whole over the water-bath in sufficient methylated spirit for the purpose. This varnish is used cold. It preserves the blade from rust, and is transparent.

TABLE CXXX.—VARNISH FOR POLISHED COPPER.

	Parts by Weight.
Sandarach	110
Rosin	30
Glycerine	5

Dissolve the two resins in sufficient spirits of wine and add the glycerine.

TABLE CXXXI.—WHITE AND BROWN HARD SPIRIT VARNISHES.

1. Best *White* Hard Varnish :—

Sandarach	60 lb.	Methylated spirit	20 gals.
Fine rosin	140 „		

2. Ordinary *White* Hard Varnish :—

Manila copal	60 lb.	Methylated spirit	28 gals.
Rosin	140 „		

3. A specially Fine *White* Hard Varnish :—

Clean sandarach	30 lb.	Methylated spirit	10 gals.
Manila	20 „	Pale rosin	50 „

Brown hard varnishes almost always contain a certain proportion of garnet shellac, but this can, with careful blending of the other resins, be reduced. In the cheapest grade of brown hard, some makers put only a small proportion of garnet shellac into the mixture and tint to a suitable brown colour by a soluble aniline dye.

TABLE CXXXII.—GIVING SEVERAL TYPICAL FORMULÆ FOR MAKING SANDARACH SPIRIT VARNISHES.

Sandarach (lb.)	50	40	20	20	20
Burgundy pitch (lb.)	70	110	50	50	30
Methylated spirit (gal.)	24	20	10	10	8

TABLE CXXXIII.—FORMULÆ FOR MORE DURABLE SANDARACH VARNISHES.

	lb.	lb.
Sandarach	30	60
Mastic	20	30
Burgundy pitch	1¼	1¼
Methylated spirit (gals.)	18	18

XII. *Shellac Water Varnishes.*—Before describing the manufacture of shellac spirit varnishes, it will be well to deal first of all with the shellac varnishes known as water varnishes and ammonia varnishes. The water varnishes are obtained by dissolving shellac in a solution of borax. One part of borax is dissolved in 20 parts of hot water; it is preferable to take distilled water; to this solution there is added, little by little, 3 parts of white shellac, taking care each time not to add any more until the previous lot is dissolved. The whole is allowed to stand, and the wax eliminated from the shellac is separated by filtration.

The solution may either be applied to *leather* already stained black, or the solution itself may be stained with aniline black before application to the leather. In either case a fine effect is obtained.

TABLE CXXXIV.—LEATHER VARNISH.

Orange shellac	3½ lb.
Borax	¾ ,,
Water	3 gals.

Boil until dissolved. Cool.

TABLE CXXXV.—REAL ENGLISH LEATHER POLISH (BLACK).

Take—

Water	22 gals.
Borax	8 lb.
Best logwood extract	4 ,,
,, shellac	24 ,,
Bichromate	3 ,,
Sal ammoniac	2 ,,

Boil up the water, and then dissolve the bichromate in about 2 gallons of it. In the remainder of the water, which is still of course being heated, dissolve first the borax and then the logwood. Then

add the shellac gradually at the boil. When the stuff has been stirred, still at the boil, for about ten minutes after the solution of the shellac, it is ready to be poured out into another vessel where the sal ammoniac is added to it and the bichromate solution already prepared. The latter is added in small portions with constant stirring. If the total weight is less than 250 lb. dilute to that with water. To be applied without brushing.

Ammonia varnish is used by *hatters* to replace the alcohol solution. Three lb. of orange shellac, 10 lb. of sal ammoniac, 6 to 8 gallons of water, are shaken in a flask. After twelve hours contact the whole is heated until completely dissolved.

The ammonia varnish, with the addition of alcohol, constitutes the *crystal varnish* used for *photographic* negatives. Alcohol would give an opaque coating, whilst ammonia gives a brilliant one. Valenta dissolves ammonia gas in absolute alcohol; to 100 oz. of this solution 8 oz. of shellac are added, and on heating on the water-bath a yellow liquid is obtained. The proportion of shellac may be increased, so as to have a better bodied varnish. If liquor ammonia be used, the coating does not dry so well.

Borax Stiffening for Hats (Ure).—Shellac 7 lb., amber rosin 1 lb., gum thus 4 oz., mastic 4 oz., borax 6 oz., copal spirit varnish ½ pint. The borax is first dissolved in a little warm water, say 1 gallon, and the solution run into a copper heated by steam, together with the resins, and boiled till of proper consistency. If it sets when run on an inclined cold slab it requires more water. When the resins seem dissolved a half-pint of wood naphtha is added and the copal varnish. The solution is then run through a sieve, when it is perfectly clear and ready for use. The comparative merits of alkaline versus alcoholic solutions of shellac in improving hats are discussed in the "Chemistry of Hat Manufacture," by Watson Smith (Scott, Greenwood & Son), pp. 63-8.

Bronze Blue Coloured Boot Water Varnish.— Shellac 10 lb., aniline blue 1½ lb., water 2 gallons. Dissolve.

Negative Water Varnish.—Bleached shellac 2 lb., borax ½ lb., soda 12½ lb., glycerine 1 to 3 oz. Make up to 2 gallons with water.

Black Leather Varnish.—Shellac 2 lb., borax 2 lb., water 1 gallon. Boil till dissolved, and then 2 lb. logwood extract and 2 lb. green vitriol in 1½ quarts of water are incorporated by boiling and constant stirring. This varnish is greenish, but dries black.

Antiseptic Water Varnish for Walls.—Borax 10 lb., caustic soda 5 lb., are dissolved in 40 gallons of boiling water and 45 lb. of shellac run into the solution with constant stirring when it is lukewarm; there are then incorporated 26 lb. of 90 per cent pure carbolic acid. Before this solution becomes thick the whole is thinned down with one-third of its volume of water.

Water Varnish for Floors.—Shellac 5 lb., soda crystals 3 lb., water 3 gallons. Boil till dissolved.

Coloured Water Varnish for Floors.—Shellac 4 lb., soda crystals

2 lb., J.F.L.S. ochre 10 lb., water 2 gallons. Dissolve the shellac and the soda in the boiling water and then stir in the ochre.

Washable Wallpaper Varnish.—Shellac or stick lac 30 lb., borax 30 lb., water 20 gallons. Boil till dissolved, filter; when applied on wallpaper with a smooth brush it dries with a fine gloss. Two coats are given; the second, after the first has dried, is applied in the same way as the first, with a smooth brush. The above varnish is for dark papers. If required for light paper the shellac is replaced by sandarach.

Marquetry Woodstains.—Dissolve 1 lb. of shellac in a gallon of water by the addition of ½ lb. of borax, and colour by the addition of about 2½ oz. of the water stain in powder. Use garnet shellac for ebony, walnut, green, rose-wood; orange shellac for oak, mahogany, blue, red, and yellow birch; bleached shellac for pine, satin-wood, maple. Any dealer in aniline dyes will supply appropriate stains.

TABLE CXXXVI.—VARNISH TO PREVENT HUMIDITY ON A PAINTING ON GLASS.

Bleached shellac	27 to 32 oz.
Borax	8 „
Carbonate of soda	2 „
Glycerine	1 to 2 „
Water	2 gals.

Dissolve borax in 1 gallon warm water, then add the borax and heat until the shellac is dissolved; allow to cool, filter, and afterwards add the glycerine and remainder of the water. Let the mixture remain undisturbed until a deposit is formed, then filter off the clear fluid for use.

Floor Polish Recipes.—The following formulæ are said to yield good floor polishes, which have the added merit of being cheap: Stearine 100 parts, yellow beeswax 25, potassium hydroxide 60, yellow laundry soap 10 parts. Water and colouring matter are added to suit. Heat together until saponification takes place. Another excellent formula is the following: Beeswax (yellow) 25 parts, yellow laundry soap 6, glue 12, soda-ash 25 parts, water and ochre a sufficient quantity. Dissolve the soda-ash in 400 parts of water; add the wax and boil down to 250 parts; then add the soap. Dissolve the glue in 100 parts of hot water, stir in the ochre and mix with the saponified wax. The following is recommended for light, unstained parquette floors: White wax 75 parts, bleached shellac 75 parts, clear rosin (transparent) 6 parts, turpentine 100 parts, methylated spirit 400 parts. Melt the wax, shellac, and rosin together, remove from the fire, let cool down somewhat, and add the turpentine with constant stirring. Warm the alcohol carefully to near the boiling-point—this must be done on a water-bath—then add to the other mixture with rapid and constant stirring. This preparation should be slightly warmed before applying, and the floor afterwards polished with woollen cloths. [All parts by weight.]

Mixture for Preserving Wood Floors.—The following is a preparation for treating the floors of factories, especially those of the engine and dynamo rooms. Five lb. beeswax are mixed with 1 lb. of potash boiled in sufficient water to thoroughly dissolve the potash. The mixture should be boiled until the water combines completely with the wax. The mixture is then taken from the fire, and a quantity of boiling water is added, stirring constantly at the same time. It will be found, if the process has been conducted properly, that 22½ gallons of water can be added to the original quantity, and the substance will still retain its homogeneous character, no clear water appearing. The mixture is then heated for five or six minutes, but is not allowed to boil. It is then taken from the fire and stirred vigorously until cool. This forms a sort of cream, which gives a brilliant polish to wood in a very little time. It should be applied with a piece of linen, and the wood then rubbed with another piece of the same material.

Floor Wax Recipes.—(1) Spermaceti 4 oz., paraffin wax 4 oz., powdered talc 8 oz. Shave the spermaceti and paraffin quite fine; mix with the talc and pass through No. 10 sieve. (2) Powdered stearine 20 oz., powdered yellow wax 5 oz., powdered soap 2 oz. (3) Yellow wax 8 oz., potassium carbonate 1 oz., oil turpentine 1 oz., water 32 oz. Heat the wax and water to boiling, add the potash, boil another minute, remove from fire, add the turpentine and stir till cold. (4) Yellow wax 5 oz., paraffin wax 2 oz., stearic acid 10 oz., oil turpentine 6 oz., benzine 7 oz. Melt together the waxes and acid, add a small quantity of burnt sienna, thoroughly mixed with the linseed oil and varnish, remove from fire and add balance of the ingredients.

TABLE CXXXVII.—VARNISH FOR RUBBER BALLOONS.

I.		II.	
Gum-arabic	8 lb.	Dextrin	7 lb.
Sugar	2 „	Glue	3 „
Water	1¼ gal.	Water	1¼ gal.

III.	
White wine	7 oz.
Senegal gum	2 „
Molasses	1½ „

XIII. *Shellac Spirit Varnishes.*—Varnishes made by dissolving shellac in methylated spirit (less frequently in wood-spirit) are widely used on wood, metal, flexible objects (e.g. leather, paper, etc.); ether, spirits of turpentine, benzol, petroleum spirit, are often added to dissolve the wax and get a clear solution, but strong alcohol is then used, 96 to 98 per cent. A clear, pale varnish is got, it is said, by stirring the varnish up for two days with white lead equal *in weight* to the shellac in solution. The varnish after settling out on standing is decanted. Bleached shellac or ordinary shellac is used according to colour desired. The former is apt to contain chlorine addition or substitution compounds, to be guarded against. Oxidizing, bleach-

ing agents render shellac much less soluble in alcohol. By covering the broken-up bleached shellac with ether and leaving it in contact therewith for twelve hours it dissolves more freely. By using 2½ lb. of shellac and upwards to the gallon of methylated spirit a turbid varnish is got, generally used as such, especially for furniture. From 1 to 3 per cent of Venice turpentine increases the elasticity. Adherence to metals is increased by not more than 0·3 to 0·5 per cent of boric acid. *Graeger's Process.*—Benzene or petroleum spirit clarifies an alcoholic solution of shellac by dissolving the wax. Graeger eliminates the wax from the shellac, but then the varnish is more brittle. He dissolves 1 lb. of shellac on the water-bath in ½ gallon of methylated spirit, and adds distilled water gradually until a cheesy mass is deposited and the liquid is clear, which occurs when the water is to the alcohol as 1 to 3. The whole is filtered through paper and washed with 67 per cent alcohol, i.e. reduced by water to a density of 0·879, and the residue dried on the water-bath until constant in weight and then dissolved in 96 per cent alcohol. Venice turpentine, Burgundy pitch, elemi are added to shellac leather varnishes after standing some days, and filtration if need be.

By using double the quantity of alcohol, shellac varnish filters more freely. In countries where excise regulations allow, the excess of alcohol may be recovered by distillation. *Common Shellac Varnishes* may be made thus: the Venice turpentine is melted till it fumes, then the shellac is added in two or three portions without stirring, as the shellac would aggregate into intractable lumps. No more is added until the mixture is fluid and homogeneous. When all the shellac is in, and the mass fluid, the pan is taken off the fire, cooled slightly, and the alcohol added. There are many recipes for elastic varnishes, all very different, but the following includes them all: Dissolve 1 lb. of shellac in 5 lb. of methylated spirit alcohol, say 1½ lb. to gallon, and add according to quality, elasticity, etc., desired, either mastic, Venice turpentine, Burgundy pitch, sandarach, benzoin, or camphor, or mixtures thereof, to the extent of 0·1 to 1·0 lb. for every lb. of shellac, as shown in the following varnishes for very different purposes:—

TABLE CXXXVIII.—SHOWING COMPOSITION OF SHELLAC SPIRIT VARNISHES FOR VARIOUS PURPOSES.

	Varnish for Bottle Capsules. lb.	Bookbinders' Varnish. lb.	Leather Varnish. Ordinary. lb.	Leather Varnish. Nubian Blacking. lb.
Shellac	1	1	1	1
Alcohol, 96 per cent	5	5	5	5
Substances to produce elasticity	0·1 Venice turpentine	0·9 Mastic, Sandarach, Camphor	1 Venice turpentine, Mastic, Sandarach	1 Camphor, Nigrosine q.s.

The colouring dissolved in a little strong alcohol is then added, e.g. alcoholic solutions of dragon's blood, gamboge, and annatto for gold lacquers. If too thick the varnish is thinned down with methylated spirit. *Iridescent Bronze Varnishes.*—Sprays, feathers, birds' wings, coloured by magenta crystals and well dried, are laid on filter paper placed above bleaching powder made into thin paste with water. The colouring matter is soon oxidized by the escaping chlorine and thus produces the iridescence.

Shellac Spirit Varnishes for Leather.—Dissolve 8 lb. of shellac and 3 lb. of wax in 15 lb. of alcohol and 2 lb. of castor oil. The whole, heated to a syrupy consistency, is applied with a brush moistened in alcohol. *Brilliant Leather Varnish.*—Digest 2 lb. of shellac in 10 lb. of methylated spirit in a closed vessel in a warm place for two to three days, stirring daily. Dissolve ¼ lb. of yellow soap in 4 lb. of hot alcohol, add ½ lb. glycerine, stir well, and add to the shellac solution. To impart lustre add ½ lb. nigrosine in 1½ lb. alcohol and let the whole stand in a warm place for a fortnight. But compositions like these are not really spirit varnishes. *Black Leather Spirit Varnish.*—Garnet shellac 15 lb., rosin 5 lb., Venice turpentine 1 lb., nigrosine 1½ lb., methylated spirit 10 gallons. *Jet Black China Varnish.*—Shellac 10 lb., turpentine 5 lb., logwood extract 1 lb., bichromate of potash 1 lb., indigo 1 lb. *Dead Black Varnish for Leather.*—Shellac 20 lb., Venice turpentine 2 lb., yellow wax 2 lb., methylated spirit 10 gallons. The mixture is heated to 70° C. (158° F.) and kept at that temperature until all is dissolved. One lb. of magnesia is stirred in, after which the solution is filtered and then mixed with 1 lb. of carbon gas black, and the bulk made up with spirit to 12 gallons. *Von Ballas' Leather Varnish.*—(A) Rosin 3 lb., sandarach 6 lb., Venice turpentine 3 lb., spirits of turpentine 3 lb. (B) Shellac 12 lb., methylated spirit 11 gallons, lampblack 1½ lb. Dissolve A by the aid of heat and run in B. *Black Varnish for "Patent" Leather.*—Garnet shellac 18 parts, dark resin 5 parts, Marseilles soap 3 parts, Venice turpentine 2 parts, are dissolved in 100 parts of 95 per cent spirit, and coloured with 1½ parts of spirit-soluble nigrosine. *Leather Varnish.*—Twelve parts of orange shellac, 1 of sandarach, 3 of Venice turpentine, 3 of colophony, 0·4 of camphor, and 4 of resin spirit, in 90 parts of 95 per cent spirit, and after being mixed with the colouring matters given below, dissolved in 10 parts of warm spirit, are clarified and filtered. Colouring matters: For black 1½ parts of spirit-soluble nigrosine; for yellow 0·6 part of spirit metanil yellow; for orange the same with 0·3 part of spirit cerotine orange R. extra, for red 0·8 part of spirit fire-red, for brown 0·6 part of spirit Bismarck brown, for green 0·8 part of spirit yellow-green. *Black Shoe Varnish.*—Sixteen parts of Manila copal, 12 of sandarach, 4 of garnet shellac, 3 of Venice turpentine, and 3 parts of castor oil, are dissolved in 100 parts of 95 per cent spirit, and coloured with 3½ parts of nigrosine, soluble in spirit and oil. *Black Leather Varnishes.*—(1) Dissolve 5 lb. camphor and 180 lb. garnet

shellac in 550 lb. of 96 per cent methylated spirit with the aid of heat. Then add 80 lb. of hot Venice turpentine and filter. While the varnish is still hot, stir in 20½ lb. of nigrosine. (2) Dissolve 13 lb. garnet shellac, and 2 lb. of sandarach in powder, in 30 lb. of 90 per cent methylated spirit with the aid of heat. Filter and add 3 lb. of pure Venice turpentine hot. Then stir in 1 lb. of nigrosine in 4 lb. of 96 per cent methylated spirit. This varnish is better for wood than for leather. (3) Dissolve 5 lb. garnet shellac, 7 lb. dark copal, 2 lb. mastic, and 2 lb. sandarach, all in powder, in 24 lb. of 96 per cent methylated spirit with the aid of heat. Then filter and add 2 lb. of pure hot Venice turpentine. Colour with 1 lb. nigrosine in 6 lb. of 96 per cent methylated spirit. (4) Dissolve 15 lb. dark copal and 5 lb. shellac both in powder in 24 lb. of 96 per cent methylated spirit with the aid of heat. Then add 2 lb. of hot pure Venice turpentine. and colour with 1½ lb. nigrosine in 6 lb. of 96 per cent methylated spirit. (5) 250 oz. shellac, 30 oz. Venice turpentine, 30 oz. nigrosine, 2 oz. Bleu de Lyon, 690 oz. methylated spirit.

TABLE CXXXIX.—SHOWING THE COMPOSITION OF VARIOUS SPIRIT VARNISHES AND COMPOSITIONS FOR LEATHER.

	A.	B.	C.	D.	E.	F.	G.	H.
Shellac in lb.	35	25	45	25	40	10	80	56
Sandarach in lb.	8	6	—	3	—	2	—	—
Rosin in lb.	8	12½	—	—	—	—	40	—
Mastic in lb.	—	—	—	3	—	—	—	—
Burgundy pitch in lb.	8	16	20	12½	7	10	—	56
Camphor in lb.	1	—	—	—	—	—	3	—
Naphthaline in lb.	—	—	14	—	5	—	—	—
Boiled oil in lb.	—	—	2	—	—	—	—	—
Castor oil in lb.	—	1	4	3	5	1	—	—
Rosin spirit in gals.	1	—	—	—	10	—	—	25
„ oil in lb.	—	12½	—	10	—	—	14	—
Spirit nigrosine in lb.	4	1	—	—	1	—	—	—
Induline in lb.	—	—	1¼	1½	—	1	—	1
Prussian blue in lb.	—	—	—	—	—	—	5	—
Methylene blue in lb.	—	—	½	¼	—	—	—	—
Lampblack in lb.	—	3	—	—	5	—	14	10
Methylated spirit, 64° O.P. in gals.	25	25	25	25	25	25	25	25
Benzene in gals.	—	—	5	—	—	5	—	—

A, black polish for "patent" leather. B, black polish for harness and coach leather, upholstery. C, imitation Nubian blacking. D, harness polish, self-shining. E, waterproof varnish for leather. F, jet black elastic varnish for leather. G, waterproof spirit black varnish for leggings.

Bookbinders' Shellac Varnishes.—(1) Shellac 10 lb., Venetian turpentine 3 to 4 lb., methylated spirits 36 lb. (2) For a colourless varnish bleached shellac 11 lb., Venice turpentine 3 lb., methylated spirit 40 lb. (3) Shellac 10 lb., spirit of turpentine 1 lb., methylated spirit 30 lb.

Shellac Varnish for Leather.—Rosin 3 lb., Venice turpentine 3

lb., sandarach 6 lb., shellac 12 lb., methylated spirit 90 lb. The filtered solution is mixed with $1\frac{1}{2}$ lb. of carbon black. The ingredients may be supplemented by up to 6 lb. of copal.

TABLE CXL.—SHELLAC VARNISH FOR LEATHER.

Shellac	40
Venice turpentine	200
Logwood extract	20
Potassium bichromate	4
Indigo carmine	3
Methylated spirit	600

The extract is dissolved in the spirit and the bichrome added. The shellac and turpentine are dissolved in the black solution, then the indigo carmine is added, which gives a bluish cast to the black varnish.

TABLE CXLI.—RED SHELLAC LACQUER FOR WHITE METAL.

	Parts by Weight.
Seed lac	20
Powdered sandarach	11
Turmeric	5
Essence of lavender	3
Red sandalwood	3
Spirits of wine	140

Reduce all these solids into very fine powder and dissolve them in the spirits of wine, either over a water-bath or over a sand-bath, the latter being preferable.

TABLE CXLII.—YELLOW SHELLAC LACQUER FOR WHITE METAL.

	Parts by Weight.
Shellac	100
Small mastic	80
Venetian turpentine	76
Dragon's blood	45
Gamboge gum	50
Spirits of wine	1500

Proceed as in the recipe above.

TABLE CXLIII.—GOLD SHELLAC LACQUERS FOR METALS.

A.

	Parts by Weight.
Sandarach	50
Seed lac	50
Venetian turpentine	24
Dragon's blood	6
Gamboge	2
Spirits of turpentine	400

This is prepared by dissolving all the solid substances in the spirits of turpentine over the water-bath.

B.

	Parts by Weight.
Sandarach	125
Seed lac	125
Dragon's blood	15
Gamboge	5
Turmeric	2
Ground glass	150
Spirits of turpentine	1000

These are dissolved as before over the water-bath, that is to say, in a jacketed pan in which the water boils in the outer case, and then 50 parts of weight of liquefied Venetian turpentine are added.

C.

	Parts by Weight.
Shellac	32
Gamboge gum	15
Saffron	15
Annatto	16
Dragon's blood	16

TABLE CXLIV.—PHOTOGRAPHIC VARNISH.

	Parts by Weight.
Bleached shellac	10
Mastic	2
Turpentine	2
Rectified spirits of wine	60

It need hardly be said that it is of the highest importance that the ingredients should be as pure as it is possible to obtain them.

TABLE CXLV.—SPIRIT SHELLAC JEWEL LACQUER.

	Parts by Weight.
Seed lac	90
Gamboge gum	80
Amber	30
Dragon's blood	2
Saffron	1
Sandalwood oil	2
Spirits of wine (95°)	600

The resins are rendered soluble in the usual manner, and the ordinary method for the preparation of varnishes is followed.

TABLE CXLVI.—SPIRIT SHELLAC GOLDEN LACQUER FOR COPPER.

	Parts by Weight.
Seed lac	170
Ground glass	100
Amber	60
Dragon's blood	30
Gamboge gum	5
Saffron	2
Boric acid	8

This is macerated in sufficient spirits of wine to cover the solid matter, and then filtered.

Blackboard Varnish.—Shellac varnish is employed to "renovate" blackboards: (*a*) Twenty-five parts of shellac and 7 parts of sandarach are dissolved in 25 parts of alcohol; 3 parts of gutta-percha are dissolved in 14 parts of spirits of turpentine; after cooling, the two solutions are mixed and incorporated with 50 parts finely pulverized emery, and 12 parts of very fine bone-black. The board is coated, the alcohol inflamed, and another coat applied. This operation is repeated five or six times, and a remarkably fine grain is got at the finish, with a beautiful, flat, lustreless surface. (*b*) Three and a half lb. of shellac are dissolved in 20 of alcohol and 5 lb. of emery added to the solution, and then 2 lb. of very fine bone-black, and the whole ground for a very long time. The varnish is applied to the board, the alcohol inflamed, and the operation repeated. (*c*) Fifty oz. of sandarach, 20 oz. of pyro copal, 100 oz. of shellac, 3 oz. Venice turpentine are dissolved in 400 oz. of 96 per cent alcohol and 40 oz. ether; to this solution there is added a mixture of 15 oz. of lampblack, 5 oz. of ultramarine blue, and 100 oz. of emery. It is not necessary to inflame the spirit. Shining spots can be removed by rubbing with amber so as to obtain a lustreless surface. Itinerant renovators of blackboards charge the unwary teacher as many shillings for renovating a blackboard as the raw materials (brown hard spirit lampblack and a little methylated spirit to fire the coating; sometimes they merely stir up the lampblack with the methylated spirit, apply the coat and fire it) cost pence at the nearest oil and colourman's shop.

French Polish.—The original formula for French polish is lost in the labyrinth of antique technical literature. The celebrated "French polish," says Hebert, "is effected by a spirit varnish, treated in a peculiar way". The following mode of preparing it and using it, he continues, may be relied upon as genuine, being extracted from that very accurate French work, the "Dictionnaire Technologique". The varnish is composed of

Sandarach	14 oz. 2 drams.
Mastic in drops	7 „ 1 „
Shellac, the yellower the better . . .	14 „ 2 „
Alcohol of 0·8295 specific gravity . . .	3 qts. 1 pint.

The resinous gums are to be pounded and their solution effected by continued agitation, without the aid of heat. When the woods to be varnished are very porous 7 oz. and 1 dram of Venice turpentine are added. In order the better to divide the resins and to cause them to present a better surface to the action of the alcohol, they should be mixed with an equal amount of ground glass, the latter preventing the dust of the resin from forming clots; the solution is thus easier made, and in less time. Before applying the varnish the wood should be made to imbibe a little linseed oil. It must then be rubbed with old flannel in order to remove the excess of oil; blotting-paper may be used for the same purpose or finely sifted sawdust. After-

wards the varnish should be applied by saturating it with a piece of old, soft, coarse linen cloth, many times folded into a sort of cushion, and rubbing it softly on the wood, turning the linen from time to time until it appears nearly dry. The linen should be saturated afresh with varnish, and the rubbing be continued in the same manner until the pores of the wood are completely filled. Care should be taken not to make the linen too wet nor to rub too hard, especially at the beginning of the operation. When the varnish sticks or becomes tacky a very small drop of olive oil is to be applied with the end of a finger, uniformly all over the cushion. The finishing is effected by pouring a little pure alcohol upon a piece of linen which is lightly rubbed over the varnished wood, and as the linen and the varnish dry the wood is rubbed briskly until it takes a beautiful polish like a looking-glass.

TABLE CXLVII.—RECIPES FOR SHELLAC SPIRIT VARNISHES.

1. BROWN POLISH.

Oxidized turps	50-80 lb.
Garnet shellac	80 „
Methylated spirit	45 gals.

2. PALE POLISH.

Orange shellac	90 lb.
Methylated spirit	45 gals.

3. DARKER POLISH.

Venice turpentine	50 lb.
Garnet shellac	100 „
Methylated spirit	45 gals.

4. WHITE POLISH.

Bleached shellac	100 lb.
Methylated spirit	40 gals.

5. FLOOR VARNISH.

Sandarach	50 lb.
Orange shellac	80 „
Methylated spirit	45 gals.

6. BOOKBINDERS' VARNISH—PALE.

Venice turpentine	40 lb.
Orange shellac	100 „
Methylated spirit	40 gals.

7. BOOKBINDERS' VARNISH—DARK.

Burgundy pitch	20 lb.
Garnet shellac	100 „
Methylated spirit	40 gals.

7A. BOOKBINDERS' VARNISH.

Shellac	$82\frac{1}{2}$ lb.
Spirits of turpentine	3 gals.
Methylated spirit	80 „

8. BOOKBINDERS' VARNISH—WHITE.

Venice turpentine	50 lb.
Bleached shellac	100 „
Methylated spirit	42 gals.

9. WHITE POLISH.

	I.	II.	III.
Bleached shellac	40	50	60 lb.
Methylated spirit	27	27	27 gals.

10. PALE POLISH.

	I.	II	III.
Bleached shellac	40	50	60 lb.
Orange shellac	10	10	10 „
Methylated spirit	27	27	27 gals.

11. PALE BROWN POLISH.

	I.	II.	III.
Orange shellac	40	50	60 lb.
Methylated spirit	28	28	28 gals.

12. BROWN POLISH.

	I.	II.	III.
Orange shellac	40	50	60 lb.
Garnet shellac	20	20	20 „
Methylated spirit	30	30	30 gals.

13. DARK BROWN POLISH.

	I.	II.	III.
Garnet shellac	40	50	60 lb.
Methylated spirit	25	25	25 gals.

14. RUSSIAN POLISHES.

	I.	II.	III.	IV.	V.	
Shellac	36	7	—	—	12	lb.
Benzoin	18	14	—	—	—	„
Mastic	9	2	2	1	3	„
Sandarach	—	3	1	4	—	„
Venice turpentine	—	—	1	$1\frac{1}{2}$	—	„
Meth. spirit	11	9	$1\frac{1}{3}$	2	$7\frac{1}{2}$	gals.

TABLE CXLVIII.—MIXED SHELLAC SPIRIT VARNISHES.

1. Shellac, orange	40 lb.	4. Garnet shellac	30 lb.
Venice turpentine	30 ,,	Burgundy pitch	30 ,,
Manila copal	50 ,,	American rosin	70 ,,
Methylated spirit	34 gals.	Methylated spirit	27 gals.
2. Shellac, orange	20 lb.	5. Bleached shellac	40 lb.
Burgundy pitch	20 ,,	Venice turpentine	20 ,,
Manila copal	50 ,,	Sandarach	40 ,,
Methylated spirit	23 gals.	Methylated spirit	23 gals.
3. Garnet shellac	40 lb.	6. Bleached shellac	20 lb.
Burgundy pitch	30 ,,	Venice turpentine	20 ,,
American rosin	50 ,,	Window glass rosin	60 ,,
Methylated spirit	27 gals.	Methylated spirit	20 gals.
7. Orange shellac	40 lb.		
Venice turpentine	150 ,,		
Sandarach	40 ,,		
Methylated spirit	12 gals.		

TABLE CXLIX.—RECIPES FOR PATENT KNOTTING AND FRENCH POLISH.

A. Good Patent Knotting.		A. Common Polish.	
Common orange shellac	100 lb.	Common orange shellac	40 lb.
Middle rosin	40 ,,	Good middle rosin	20 ,,
Methylated spirit (64 O.P.)	24 gals.	Methylated spirit (64 O.P.)	20 gals.
B. Fine Patent Knotting.		B. French Polish.	
Orange shellac	125 lb.	Common orange shellac	60 lb.
Methylated spirit (64 O.P.)	25 gals.	Methylated spirit (64 O.P.)	30 gals.
Oxalic acid[1]	½ lb.	Oxalic acid[1]	½ lb.
C. Finest Patent Knotting.		C. Best French Polish.	
Good (TN.) orange shellac	120 lb.	Orange shellac (TN.)	60 lb.
Methylated spirit (64 O.P.)	24 gals.	Methylated spirit (64 O.P.)	24 gals.
Oxalic acid[1]	¾ lb.	Oxalic acid[1]	1 lb.
		D. Finest Superior French Polish.	
		Finest pale orange shellac	60 lb.
		Methylated spirit (64 O.P.)	24 gals.
		Oxalic acid[1]	½ lb.

The following is a process for making French polish and spirit furniture varnish in a small way :—

			s.	d.
(1) Methylated spirits	1 gal.	cost	3	6
Shellac	1½ lb.	,,	1	9
Gum benzoin	½ ,,	,,	1	3
,, sandarach	½ ,,	,,	0	6
,, thus	¼ ,,	,,	0	1
Resin	¼ ,,	,,	0	1
Yield, 1⅓ gallons costing			7	2
Or say, 5s. 6d. per gallon.				

[1] Oxalic acid is used to destroy the violet to black coloration which the natural dye left in shellac gives with metals, solder, etc., lead, iron, and tin. It may also assist in the polishing of the wood. Needless to say, no such acid spirit varnish should be used on metals.

(2) Methylated spirits 1 gallon, shellac 2 lb., benzoin ½ lb., rosin 1 lb. (3) Spirits 1 gallon, shellac 1 lb., sandarach ¾ lb., mastic ¾ lb. (4) Spirits 1 gallon, mastic ½ lb., rosin 2 lb., benzoin 3 lb. Nos. 2 and 3 are useful for fancy goods, No. 4 for musical instruments. (5) Furniture varnish : spirits 1 gallon, shellac 1 lb., sandarach 1 lb., benzoin ½ lb., Venice turpentine ½ lb. (6) Paper varnish for screens, etc. : equal quantities of Canadian balsam and rectified oil of turpentine. (7) Spirits 1 gallon, copal 2 lb., camphor ¼ lb., mastic ½ lb. Dissolve, then add Venice turpentine ½ lb. (8) For carved cabinet work : shellac 2 lb., rosin 1 lb., spirits 1 gallon. Apply warm.

Methylated spirit is given in all cases as the solvent, as being more pleasant to use. Should the weather or room be damp, or a quicker varnish be required, wood naphtha may be used instead, which gives what is termed naphtha varnish.

Continental Polishes.—All shellac polishes are solutions of shellac in alcohol to which other resins, such as mastic, sandarach, etc., are often added. The use of this polish is characterized by the fact that it is rubbed on and not applied with a brush. As just mentioned, the principal constituents are shellac and alcohol. In making the polish alcohol should be chosen containing as little water as possible, and the shellac should be of the best orange variety. If the latter is hard to come by it may be necessary to put up with garnet shellac, which, however, gives a distinctly darker polish. This, however, can be avoided by using bleached shellac and mixing bleached and unbleached shellac in such proportions as to give the desired colour. The polish used by joiners and furniture makers is mostly made from pale shellac. A continental writer complains that the darker and cheaper sorts of shellac have their colour lightened with sulphide of arsenic. This adulteration is readily detected by the garlic smell produced when such shellac is burnt. But both rosin and orpiment in shellac have in moderation a legitimate function. Adulteration with rosin is another grievance. Water-free ether will only dissolve about 6 per cent of pure shellac and chloroform about 10 per cent. If the numbers are higher the addition of rosin may be suspected. Various attempts have been made to purify shellac varnish otherwise than by filtration, but without success. Boiling with water has been tried, and also treatment with lime, caustic soda, or ammonia, but no result follows. Small quantities of shellac polish may be filtered through a piece of felt, but for large amounts a filter press is necessary. The so-called earth shellac from Australia (*Gummi accroides*) (pp. 235-7) should not be used for polishing, although it will serve for ordinary varnish. The following are some recipes for "polishes":—

German "Polishes".—1. The "polish" most in use is the so-alled 12 per cent polish—so called because it consists of 12 per ent of shellac and 88 per cent of alcohol.

2. A more lustrous "polish" for wood is prepared by dissolving lb. of shellac and 1 lb. of sandarach in 30 lb. of alcohol and ltering.

3. An equally lustrous "polish" is prepared by dissolving 1 lb. of mastic in 56 lb. of alcohol, and then adding 4 lb. of linseed oil. The oil makes this polish very elastic (a sort of megilp).

4. Take 4 lb. of shellac, 50 lb. of alcohol, 1 lb. of dragon's blood, and a little turmeric—about ¼ oz. This "polish" adheres well to metal.

5. Dissolve 2 lb. of sandarach, 2 lb. of mastic, 2 lb. of white shellac, and 4 lb. of garnet shellac in 75 lb. of alcohol.

6. Dissolve 7 lb. of anime, 7 lb. of sandarach, 60 lb. of benjamin in 450 lb. of alcohol. Filter, and add 32 lb. of poppy oil. To be shaken before use.

7. A very lustrous "polish" is prepared by dissolving 3 lb. of sandarach and 12 lb. of benjamin in 100 lb. of alcohol.

8. A "polish" to be applied with a brush is made by dissolving 3 lb. of shellac and 3 lb. of refined rosin in 25 lb. of alcohol.

9. Dissolve 1 lb. of mastic and 2 lb. of shellac in 10 lb. of alcohol, and filter. This is also applied with a brush.

A German French Polish.—Horn attempts to facilitate the operation by using a polish that will quickly absorb the oil left upon the furniture by the preliminary polishing. In polishing furniture in the ordinary method, it is first rough-polished with one of the usual polishes, and afterwards finished off by being polished with spirit or alcohol. This final polish with spirit or alcohol is a very laborious and tedious operation, since the spirit or alcohol does not readily dissolve the oils and fat left upon the furniture by the first or preliminary polishing. His new and improved furniture polish is prepared by mixing in about the following proportions the materials mentioned: 240 of alcohol, such as methylated spirits, are intimately mixed with 120 of acetone, and slightly heated. In this mixture 8 of benzoin and 16 of sandarach are completely dissolved. After this solution has been carefully filtered, 440 of benzine are added, and intimately mixed therewith by shaking.

A perfectly clear liquid is produced, ready for use as a finishing polish, and the high percentage of benzine which it contains dissolves very quickly the fats remaining from the rough-polishing, so that by the use of this liquid a very highly polished surface on the article treated can be produced in a very short time. It is stated that the high degree of polish is very lasting, and the polished surface is not liable to become cracked or to assume a dull appearance.

Varnish Compositions for Fine Furniture.—Gustav Tüschel, Odessa, has patented the following: (1) Composition for painting pianos, billiards, or other fine furniture consisting of 140 gr. of stick lac and 20 gr. of white bleached shellac, both pulverized, 3 gr. of transparent French colophony, pounded, 8 gr. of benzoin gum of Sumatra, 5 gr. of benzoin gum of Siam, both of the latter ground, 8 gr. of camphor in corns, pounded. These products are placed in an iron kettle, and are heated and mixed. When this is done the composi-

tion is allowed to cool, then an addition is made of 12 gr. sulphuric ether and 15 gr. ground cornelian; then this mass is thoroughly pressed and dried during three days. After these three days the mass is put into a barrel wherein there is added 1000 gr. of methylated alcohol of 95° to 96°, whereupon the barrel is well closed and turned during six hours. Then the barrel is allowed to rest three days, after which time the liquid obtained is filtered and racked off into bottles. When painted with this composition white raw wood becomes like real mahogany, and it has the advantage that the furniture that has been polished with it can be washed with water without losing its brilliancy, and that it does not swell in damp rooms. (2) For black ebony varnish the proceedings are as follows: The operation is the same as under No. 1, but when the addition of sulphuric ether is made, there is added 20 gr. aniline black instead of 15 gr. ground cornelian. It is used for painting raw white-wood furniture, to which it gives the appearance of real ebony. (3) Natural brown quick varnish is produced as follows: Its fabrication being the same as in No. 1, but without any addition of any ingredient when mixing the composition with sulphuric ether; it is used for painting raw white-wood furniture, and giving it the look of natural wood furniture. (4) Varnish for pianos, billiards, and other fine furniture, produced as follows: The operation being the same as in No. 1, although there is heated and mixed 120 gr. ground stick lac, 100 gr. sand lac, 12 gr. French colophony, 8 gr. benzoin gum of Siam, 30 gr. ground gum mastic, 20 gr. cornelian. Further, instead of 1000 gr. alcohol, there is only added 600, then the barrel is turned during an hour, whereupon the liquid allowed to rest six days instead of three days. (5) Varnish for pianos, billiards, and other fine furniture of palisander, consisting of 120 gr. sandarach, 100 gr. ground stick lac, 30 gr. ground gum mastic, 45 gr. Venetian turpentine, 20 gr. pounded white bleached shellac, 20 gr. cornelian, 6 gr. aniline black. Further, there is added 12 gr. of ether, and afterwards 600 gr. of methylated alcohol.

A German Furniture Polish.—Guaicum 125 parts, benzoin 125 parts, shellac 30 parts, linseed oil 150 parts, benzine 30 parts, alcohol, wood-spirit, 3000 parts. Mix and dissolve. The polish is applied with a sponge or brush and the object is let stand for a half-hour. A linen cloth moistened with oil is then used as a rubber, and a brilliant polish is obtained which is said to be very lasting, and is unaffected by water or other substances which usually injure varnish. Another advantage of it is that it may be applied to woods that have never been varnished or polished, and gives a result equal to the best French polish. No skill is said to be requisite in its use. The rubber must be of linen, and oiled only sufficiently to prevent its sticking when first applied.

The best basis for furniture varnish is undoubtedly shellac and methylated spirit, say 2 to $2\frac{1}{2}$ lb. shellac to 1 gallon spirit, but shellac alone is rather too hard, therefore it is advisable to soften

it, hence the addition of a small quantity of linseed oil (raw 4 oz.) or gum elemi ($\frac{1}{2}$ lb.). Shellac is dear, but it is difficult to replace it with cheaper resins, as these lack the good qualities of shellac. Try 1 lb. shellac, 1 lb. window-glass resin, 4 oz. soft Manila copal, 4 oz. raw linseed oil, 1 gallon spirit—all mixed together at one time. Should this prove too thin, add a little more shellac or some gum sandarach. This varnish will also do as a basis for cycle blacks, adding a little vegetable black and spirit black to colour it, and 4 oz. boiled linseed oil to the gallon. For straw-hat polishes it is a little too stiff; the proportion of shellac should be reduced, replacing it by a mixture of soft Manila copal and elemi, colouring with spirit black or Bismarck brown or chrysoidine or other aniline dye.

TABLE CL.—REH'S BASIS SPIRIT VARNISHES.

Ref. Letter.	Resin.	Resin in lb.	Meth. Spirit, Gals.	Ref. Letter.	Resin.	Resin in lb.	Meth. Spirit Gals.
A	Sandarach	33	8	E	Stick lac	33	8
B	Bleached shellac	26	9	F	Manila copal	33	8
C	Orange shellac	26	9	G	Rosin, good strained or H	50	7
D	Garnet shellac	33	8	H	Rosin J	50	6

1. *Reh's Essence of Camphor for Imparting Elasticity to Spirit Varnishes.*—2 lb. of camphor to 3 lb. of methylated spirit.

2. *Reh's Turpentine Extract* I. *for same purpose.*—8 lb. Venice turpentine, 2 lb. methylated spirit.

3. *Reh's Extract of Benzoin.*—1 lb. benzoin, 2 lb. methylated spirit.

The above varnishes and extracts are used as follows:—

For yellow polish use stock varnish C.

For white polish use stock varnish B.

For mahogany and ebony use stock varnishes D and E.

For black polish use stock varnish C.

The essence of camphor and the extract of benzoin are added to quick-drying varnish. According as the proportion of these is larger or smaller, the shorter or longer will be the time occupied in drying. In making leather varnishes (which should not contain rosin nor stock varnish A) from the above stock spirit varnishes, use as much as 20 per cent of (mostly) turpentine extract with the shellac stock spirit varnishes B, C, D, and E. But when varnishes B, C, D, E are mixed with F, G, and H, only 10 per cent of extract is added. For wood, A, B, C, D, E may contain 10 per cent extract; F, G, H, 5 per cent.

TABLE CLI.

	I. lb.	II. lb.	III. lb.	IV. lb.	V. lb.	VI. lb.	VII. lb.
Basis varnish B	—	500	—	—	80	—	—
,, C	500	500	—	—	—	35	—
,, D	—	—	250	—	—	—	50
,, F	—	—	—	70	—	—	—
,, G	—	—	500	—	—	10	—
Camphor essence	5	25	—	20	10	—	2
Turpentine extract	25	—	—	—	—	7	—
Benzoin extract	20	—	—	—	—	—	—
Castor oil	—	5	—	—	5	—	2
Copal oil	—	10	—	—	3	—	1
Mother varnish VI.	—	—	250	—	—	—	—
Turps	—	—	—	10	—	—	—
Lavender oil	—	—	—	—	2	—	—

I. and II. Russian polish; III. cask glaze; IV. V. metal varnish; VI. leather varnish; VII. floor varnish (a similar varnish may be made from basis varnish G or H).

TABLE CLII.—REH'S ORANGE AND YELLOW LACQUERS.

	lb.	lb.
Basis varnish	95	95
Coralline solution	4	3
Picric acid	½	2
Turmeric solution	½	—

Paper Varnishes.—A, B, F, H, 20 per cent of camphor or turpentine extract being added to A and B and 10 per cent to F and H.

TABLE CLIII.—VARIOUS MIXED SHELLAC VARNISHES.

Resins and Solvents.	Parisian Wood Varnish. lb.	St. Petersburg Wood Varnish. lb.	Sculptors' Varnish. lb.
Shellac	25	7	25
Sandarach	25	20	26
Venice turpentine	12	—	10
Mastic	6	—	—
Galipot	—	5	10
Benzoin	—	2	5
Rosin	—	5	—
Camphor	2	1	2
Lavender oil	2	—	2
Methylated spirit (gals.)	14½	13½	14½
Ether, rectified (lb.)	—	3	—

TABLE CLIV.—RECIPES FOR GILT-CORNICE LACQUERS.

	A.	B.
Dragon's blood (in lb.)	½	—
Gamboge (in lb.)	4	3
Alcoholic extract of sandalwood (in pints)	½	½
Shellac (in lb.)	7½	20
Best Australian sandarach (in lb.)	7½	5
Venice turpentine	2½	2½
Methylated spirit (in gals.)	11	10

N.B.—A flat; B paler and more brilliant; 20 lb. of finely pulverized talc are incorporated with B, after which the solution is strained.

Golden Beetle Lacquer.—Diamond fuchsine 8 lb., methyl violet 4 lb., Sumatra benzoin 10 lb., methylated spirit 10 gals. Dissolve the Sumatra benzoin in a portion of the spirit and filter; dissolve the dyes in the other portion; mix, and filter once more if need be.

Mastic Polish.—Shellac 50 lb., mastic 13 lb., methylated spirit 27 gals. *Varnish for Microscopic Work.*—Shellac 6 lb., castor oil 2½ lb., methylated spirit 3 quarts. *Gold Varnish for Opticians.*—Shellac 14 lb., aniline yellow MN. 1 lb., aniline orange 1½ oz., methylated spirit 4 gals. *Collodion Negative Varnish.*—Bleached shellac 8 lb., orange shellac 1 lb., sandarach 1 lb., methylated spirit 7 gals. *Universal Varnish.*—Shellac 15 lb., mastic 2 lb., methylated spirit 11 gals. *Schefold's Negative Varnish.*—Bleached shellac 30 oz., mastic 10 oz., Venice turpentine 1 oz., methylated spirit 350 oz. *Moody's Polish.*—Shellac 15 lb., benzoin 5 lb., dragon's blood 11½ lb., acetone 10 gals.

TABLE CLV.—SPECIAL POLISHES.

Shellac	6	36	10½
Benzoin	—	18	21
Mastic	1¼	9	8
Methylated spirit	3¾	12	13½

Brilliant Varnish for Photographers.—Beeswax 100 oz., elemi 16½ oz. Dissolve in as much of an alcoholic solution of shellac as may be necessary.

TABLE CLVI.—SOME AMERICAN SPIRIT VARNISHES.

A. WHITE SHELLAC.

Bleached shellac	3 to 4 lb.
Sulphuric ether	enough to dissolve wax
95 per cent grain alcohol	enough to make 1 gal.

B. LIGHT ORANGE SHELLAC.

	Ord.	Med.	Heavy.
Lt. unbleached shellac	3 lb.	3½ lb.	4 lb.
95 per cent grain alcohol, or Columbian spirits, commercially pure methyl alcohol	5¾ pts.	5½ pts.	5¼ lb.

C. MEDIUM ORANGE SHELLAC, No. 2.

Orange shellac	100 lb.
95 per cent grain alcohol	21 gals.

Slowly mix No. 1 with No. 2, stirring well. Makes very heavy body goods.

D. COFFEE BOX SHELLAC.

Neut. rosin	150 lb.
95 per cent grain alcohol	15 gals.
Dissolve and add grain alcohol shellac	20 „

E. RE-TOUCHING SPIRIT VARNISH.

Pale shellac	95 parts
Sandarach	190 „
Neut. W.W. rosin	125 „
95 per cent grain alcohol	1000 „

Agitate warm.

Bronze Shellac Spirit Varnish for Iron.—Add 112 parts, by weight, of shellac and 14 parts benzol to 500 parts methyl alcohol. Put the bottle in a warm place and shake the mixture frequently. When the shellac is dissolved, leave the bottle in a cool place for two or three days till the solution is clear; pour the clear fluid into another bottle, and well cork the latter in order that the contents may be fit for use on the most delicate work. Add sufficient methylated spirit to the sediment remaining in the first bottle for the mass to be easily taken up with a brush, and pour the mixture through a thin cloth. This mixture may be used as a priming and for coarse articles. If it is desired to make a paint, mix as much green bronze powder as necessary with the proper quantity of the second fluid. To alter the shade, a little lampblack may be mixed in for dark colours, red and yellow ochre for brighter colours. The iron which it is desired to paint must be clean and smooth, and the paint applied thin and with a soft brush. When the first coating is dry, a second is added, and the application renewed till a nice, uniform bronze surface has been obtained. The portions in relief should be painted very gently with the free varnish and gold bronze applied; when completely dry, spread a thin layer of varnish once more over the whole.

Brown Varnish for Metals.—An excellent and quickly-drying brown varnish for metals is made by dissolving 20 oz. of kino and 5 oz. of benzoin in 60 oz. of the best cold methylated spirit; 20 oz. of common shellac, and 2 oz. of thick turpentine in 36 oz. of methylated spirit also give a very good varnish. If the brown is to have a reddish tint, dissolve 50 oz. of garnet shellac, 5 oz. balsam of copaiba, and 2 to 5 oz. of aniline brown, with or without ½ to 1 oz. of aniline violet, in 150 oz. of methylated spirit.

TABLE CLVII.—VARNISH FOR COPPER-PLATE ENGRAVINGS.

	lb.
Bleached shellac and sandarach, each	10
Mastic and camphor, each	4
Methylated spirit	100

TABLE CLVIII.—VARNISH FOR METALS.

Bleached shellac and sandarach	10
Mastic	5
Amber (fused)	5
Methylated spirit	100

Shellac dissolves in a mixture of 70 parts of carbon tetrachloride and 25 to 30 parts of 95 per cent alcohol. Sandarach and mastic are soluble in mixture 80 to 90 parts carbon tetrachloride and 10 to 20 parts of alcohol. With larger quantities of 95 per cent alcohol,

shellac is completely dissolved, and any insoluble resin more or less carbon tetrachloride may be used with the ordinary varnish solvents so as to produce two sorts of varnish, one kind for applying with the brush, the other for dipping, the great volatility of carbon tetrachloride unfitting it for use with the brush, but when dipped the yield is a brilliant uniform coat. Andes adds about 10 per cent oil varnish to the solvents which quickly clarify.

XIV. *Spirit Varnish Enamels for Machinery.*—Coloured lacquers or spirit varnish enamels are now used in painting machinery in place of oil paints sometimes varnished over. Spirit varnish enamels have no affinity for lubricating oils like paints made from linseed oil and its substitutes. A good spirit varnish enamel for applying to machinery should possess great covering or obliterative power, great lustre and the maximum of adhesive power and durability. They must be sufficiently viscous to give both gloss and resistance, and neither run in streams nor form streaks when applied. It must, moreover, be viscous enough to prevent caking at the bottom of the tin. The pigments used in spirit varnish enamels must be of as low a specific gravity practicable, which debars barytes. The pigments must be finely ground; gritty pigments mar the lustre, cover or obliterate badly, and dry with a coarse surface. The pigment is ground with, incorporated in, and amalgamated with the varnish in a ball paint mill, so that each minute particle of pigment is surrounded with and enveloped in its own film of varnish. The finished product is strained through coarse canvas to retain any grit or core. The spirit enamel varnish may be made from shellac or Borneo copal, Accra or Angola dust, acaroid resin (Australian grass-tree gum, with rosin, oleoresins, or linoleic acid as cheapening ingredients). Rosin hardened by ozone can also be used. The varnish is made either by the warm or cold process and the whole filtered to remove solid impurities. Alcoholic solutions of shellac do not filter well, but strain readily.

TABLE CLIX.—ENAMEL VARNISHES FOR WHITE AND DELICATE COLOURS.

A.	lb.	B.	lb.	C.	lb.
Sandarach	10	Manilla	10	Orange shellac	10
Thick turpentine	3	Thick turpentine	3	Thick turpentine	3
Spirit	20	Spirit	18	Spirit	40

A and B for white and delicate colours; C for all shades.

Recipe for Label Varnish.—A varnish that will resist the action of water, alcohol, oils, and dilute acids, consists of a compound made when gelatine is acted upon by formaldehyde. When the label has been pasted upon the bottle allow it to dry, then coat it with collodion to protect the ink from the action of the coating proper. This consists of a coating of a 20 per cent solution of gelatine, which, while still moist, is brushed with formaldehyde, the latter hardening with the gelatine to an almost indestructible compound. Occasionally this coating should receive a dressing with formaldehyde, to keep the coating perfectly hard and insoluble. This should be about 20 per

cent strong, but it is not necessary to remember the strength, as it should be of such consistency that it will brush nicely; it should be about as stiff as honey, and it should be put on warm. It can be put on cold, but if it is the solution would have to be a little thinner, and a little weaker in strength. After you have put on the gelatine solution, wait until it hardens, but not until it is perfectly hard. When it ceases to be liquid, paint it over with formaldehyde, full strength. In a few minutes the gelatine will harden, and after a half-hour or so the label will be coated with a film that is almost glassy with its hardness. This varnish is not affected by water, alcohol, or acids.

TABLE CLX.—SPIRIT VARNISHES FOR ENAMELS.

(a) Shellac 80 lb., thickened turpentine 50 lb., methylated spirit 43 gals.
(b) Sandarach 140 lb. thickened turpentine 60 lb., methylated spirit 40 gals.
(c) Mix 10 gals. of (a) with 12 gals. of (b).

Colour.	Pigment (in lb.).	Spirit Varnish (in gals.).	Colour.	Pigment (in lb.).	Spirit Varnish (in gals.).
Black—			Reds—		
1. Lampblack	4	8 (c)	15. Chrome red	40	12 (c)
Blues—			16. Vermilion	25	11 (c)
2. Ultramarine	30	10 (a)	17. Red lead	15	12 (c)
White lead	10		Vermilion	25	
3. Ultramarine	30	8 (c)	Browns—		
White lead	2		18. Manganese brown	40	10 (c)
4. Prussian blue	20	7 (c)	19. Umber	45	10 (a)
White lead	5		20. Raw sienna	35	10 (c)
Yellows—			Greys—		
5. Chrome yellow	30	10 (c)	21. White lead	35	10 (a)
6. Fine yellow	40	11 (c)	Lampblack	5	
7. Ochre	60	10 (a)	22. White lead	35	12 (c)
8. Satin ochre	60	11 (a)	Lampblack	5	
Orange—			Ultramarine	10	
9. Chrome orange	40	11 (c)	23. White lead	30	12 (c)
10. Red lead	35	14 (c)	Lampblack	5	
Chrome yellow	20		Ultramarine	1	
Greens—			24. White lead	40	13 (c)
11. Chrome green	30	10 (c)	Graphite	5	
White lead	10		25. White lead	40	14 (c)
12. Chrome green	40	10 (c)	Lampblack	5	
13. Zinc green	40	11 (c)	Graphite	10	
14. Zinc green	20	14 (c)	White—		
Chrome green	20		26. White lead	35	10 (b)
White lead	15				

(a), (b) and (c) refer to varnish whose formula is given above.

Varnish for Wickerwork.—Dammar varnish is often used for varnishing wicker baskets and similar goods, though quite unsuitable for this purpose, being softened by the heat of the hand. Cheap so-called copal varnishes, consisting of resin dissolved in turps, are

equally unsuitable, since they never dry hard. Consequently both varnishes should be discarded and replaced by one or other of the following, the goods being first primed with hot size to close up the pores and form a smooth ground for the varnish :—

Brown Spirit Varnish for Basketware.—A filtered solution of 2 parts of ruby shellac in 9 parts of 95 per cent spirit.

Fine Brown Basket Varnish.—Venice turpentine 1½ parts, and 1½ parts of fine orange shellac, warmed till fluid, and then slowly incorporated with 8 parts of 95 per cent spirit by stirring.

Black Spirit Varnish.—The above brown varnish is shaken up with 2 per cent of aniline black until all the latter has dissolved.

White Spirit Varnish.—Finest washed sandarach 1 part, dissolved in 2½ parts of 95 per cent spirit and mixed with ½ part of previously melted Venice turpentine. This when filtered gives a water-white quick and hard-drying varnish.

Quick-drying Copal Varnish.—One part of melted Manila copal is mixed with ¼ part of quick-drying boiled oil, followed by 1½ parts of turps, and strained through a coarse cloth, being afterwards left to stand several days. If too thick it can be thinned with turps.

TABLE CLXI.—VARNISHES FOR STRAW POLISHES.

	A.	B.	C.	D.
Orange shellac	—	—	2	4
Bleached shellac (in lb.)	2	—	2	—
Sandarach (in lb.)	—	4	—	—
Elemi (in lb.)	1	1¼	1	—
Thickened turpentine (in lb.)	—	½	—	—
Venice turpentine (in lb.)	—	—	—	1½
Methylated spirit (in gals.)	1	1¼	1	1½

A and B are for delicate tints; C for pale and D for dark colours.

Straw Hat Polishes.—The hats on which the polishes are to be applied, should be clean, free from dirt and grease. It would be worth while to give them a good scrubbing with a little warm soap and soda water, then a good rinsing in clean warm water. Lastly, they must be dried, and this should be thoroughly done, as no good results can be obtained with a damp hat.

The requirements of a hat polish are that it shall dry fairly quickly, leave some polish, be of a good colour, and dry with a coat that is not too brittle, as then it will chip off badly in wear, and show the original colour of the hat below. This is a fault which some hat polishes have. The brittleness, which is inherent in the use of a polish made from spirit and shellac, or spirit and gum sandarach only, can be removed by the addition of a little castor oil or raw linseed oil. The following recipes show how some useful colours can be got :—

Black.—This is by far the most important, and the best is got by mixing 2 oz. spirit ebony black, 1½ lb. shellac, 2 oz. castor oil, and

2 oz. raw linseed oil in 1 gallon methylated spirit. If this should come up a little too blue in shade, add a little brilliant green.

Mahogany.—Half ounce Bismarck brown R, 1½ lb. shellac, 2 oz. castor oil, 2 oz. raw linseed oil, and 1 gallon methylated spirit. By adding a small quantity of nigrosine or spirit black the shade of brown may be varied.

Bright Green.—Half-ounce brilliant green, ½ oz. thioflavine T or auramine O, 1½ lb. gum sandarach, 1 oz. castor oil, 1 oz. raw linseed oil, and 1 gallon of methylated spirit. By varying the proportions of the green and the yellow, a very great range of greens, from a yellowish-green to a bluish-green, can be got.

Maroon.—This can be got from 1 oz. safranine, ½ oz. spirit induline, 1½ lb. gum sandarach, 1 oz. castor oil, 1½ oz. raw linseed oil, and 1 gallon of methylated spirit.

Violet.—One ounce methyl violet 2B, 1½ lb. gum sandarach, 1½ oz. castor oil, 1½ oz. raw linseed oil, and 1 gallon methylated spirit. There are various brands—3R to 6B—of the methyl violets, and by using one or other of these violet polishes of various hues, from a red violet to a fine blue violet, can be made.

Varnishes for Pencil Drawings.—(1) Sandarach 10, 95 per cent alcohol 90. (2) Dammar 10, alcohol 90. (3) White gum lac 5, Venice turpentine alcohol 90. (4) Caoutchouc 2, sandarach 8, turps 45, benzol 45. (5) Gutta-percha 2, white gum lac 8, benzol 40, oil of turpentine 50. (6) Gutta-percha 3, copal 7, boiled oil 10, turps 80. (7) Caoutchouc 1, dammar 35, chloroform 6, benzine 250, a little sodium silicate being added to neutralize the acidity of the resins. (8) An ammoniacal solution of casein containing 10 per cent of calcium tannate.

Valenta's Varnishes for De Luxe Illustrations. — (1) Dammar varnish 60 oz., Venice turpentine 30 oz., Canada balsam 15 oz., copal varnish 8 lb., bergamotte oil 8 oz. (2) Copaiba balsam 24 oz., linseed oil 17 oz., rosin 37 oz., benzoin 1 oz., tolu balsam ⅝ oz. (3) Copaiba balsam 17 oz., linseed oil 8 oz., rosin 23 oz., amygdaloid benzoin 0·6 oz., tolu balsam 0·4 oz.

TABLE CLXII.—WEIGHT IN LB. OF RESINS AND DYES FOR LACQUERS PER 10 GALLONS OF METHYLATED SPIRIT.

	YELLOWS.			BROWNS.	
1.	Seed lac	20	7.	Garnet shellac	20
	Gamboge	5		Dragon's blood	10
2.	Orange shellac	20	8.	Garnet shellac	20
	Turmeric extract	5		Bismarck brown	1¼
3.	Orange shellac	20			
	Saffron	4		BLACKS.	
4.	Garnet shellac	20	9.	Orange shellac	20
	Naphthol yellow	1¼		Spirit black	2
			10.	Orange shellac	20
	BLUES.			Burgundy pitch	8
5.	Orange shellac	20		Australian sandarach	20
	Alkali blue	1¼		Nigrosine	½
			11.	Orange shellac	40
	VIOLETS.			Burgundy pitch	40
6.	Orange shellac	20		American rosin	20
	Aniline violet	2½		Nigrosine	3

Blacks (*continued*).

12.	Orange shellac	40
	Burgundy pitch	40
	American rosin	20
	Nigrosine	8

Reds.

13.	Orange shellac	20
	Spirit scarlet	1½
14.	Orange shellac	20
	Magenta	1½
	Martin's yellow	½
15.	Orange shellac	20
	Magenta	1
	Orleans	½

Reds (*continued*).

16.	Orange shellac	20
	Diamond fuchsine	1½
	Turmeric extract	10

Greens.

17.	Orange shellac	20
	Brilliant green (oz.)	10
18.	Orange shellac	20
	Brilliant green (oz.)	10
	Chrysoidine (oz.)	10
19.	Orange shellac	25
	Brilliant green	2½
	Naphthol yellow base	1

The following are best dyestuffs and the quantities required to produce very deep shades when mixed with 10 galls. of the finished spirit varnish: Spirit blue, C.I. ½ lb., Victoria blue, B.S. ½ lb., brilliant green ½ lb., imperial green ½ lb., methyl violet ½ lb. There are many brands of this dye distinguished as 7B, B, 3R; by means of these brands quite a range of variously tinted varnishes, from a pure violet with the 7B, to a purple with the 3R, can be got. Bright pink, rhodamine B ½ lb., safranine ½ lb., crimson spirit red B 1 lb., scarlet, spirit scarlet 1 lb., spirit quinoline yellow 1 lb., orange chrysordine 1 lb., Bismarck brown 2 lb., mahogany brown 2 lb., deep blue induline spirit soluble ½ lb., black spirit nigrosine or spirit black 2 lb.

TABLE CLXIII.—CONTINENTAL BOOKBINDERS' VARNISHES.

1.	Light brown varnish—	
	Refined pale shellac	5 oz.
	Venice turpentine	2 "
	Spirits of wine	16 "
2.	Dark brown varnish—	
	Refined dark shellac	10 "
	Venice turpentine	5 "
	Spirits of wine	34 "
3.	White varnish (A)—	
	Bleached shellac	11 "
	Venice turpentine	5 "
	Spirits of wine	85 "
4.	White varnish (B)—	
	Sandarach	10 "
	Venice turpentine	7 "
	95 per cent spirits of wine	84 "
5.	Varnish for full calf extra—	
	Shellac	8 "
	Sandarach	8 "
	Mastic drops	2 "
	Venice turpentine	2 "
	90 per cent spirits of wine	60 "
	Brush lightly over the book.	
6.	Elemi	4 "
	Mastic	4 "
	Sandarach	6 "
	Venice turpentine	3 "
	Spirits of wine	30 "
7.	Shellac	20 "
	Venice turpentine	2 "
	Spirits of wine	60 "
8.	Dragon's blood	2 oz.
	Gamboge	20 "
	Sandarach	4 "
	Shellac	40 "
	Venice turpentine	10 "
	Spirits of wine	200 "
9.	Mastic	5 "
	95 per cent spirits of wine	5 "
	Ether	10 "
10.	Mastic	6 "
	Sandarach	6 "
	95 per cent spirits of wine	25 "
	Ether	13 "
11.	Pyrocopal	5 "
	Mastic	2 "
	95 per cent spirits of wine	8 "
	Ether	5 "
12.	Shellac	54 "
	Venice turpentine	2 "
	95 per cent spirits of wine	344 "
13.	Shellac	63 "
	Sandarach	130 "
	Venice turpentine	15 "
	95 per cent spirits of wine	790 "
14.	Sandarach	191 "
	Venice turpentine	46 "
	95 per cent spirits of wine	763 "
	Varnish for maps—	
15.	Pyrocopal	24 "
	Essence of lavender	3 "
	Venice turpentine	14 "

Varnishes for Coating of Crayon Drawings.—(1) Sandarach 10 parts, alcohol (95°) 90 parts. (2) Manila copal 10 parts, alcohol 90 parts. (3) White gum lac 5 parts, Venice turpentine 5 parts, alcohol 90 parts. (4) Caoutchouc 2 parts, sandarach 8, oil of turpentine 45, benzol 45 parts. (5) Gutta-percha 2 parts, white gum lac 8, benzol 40, oil of turpentine 45 parts. (6) Gutta-percha 3 parts, copal 7, raw linseed oil 10, oil of turpentine 80 parts. (7) Caoutchouc 1 part, dammar 35, chloroform 6, benzine 250 parts, a little sodium silicate being added to neutralize the acidity of the resin. (8) An ammoniacal solution of casein, containing 10 per cent of calcium tannate.

Photographers' Spirit Varnishes.—Special qualifications are required in a varnish for photographic negatives. It must, of course, be colourless, hard, and impermeable, but yet elastic and powerfully adhesive. If it is deficient in hardness it will become damaged by the printing of positives from it, and if it is not sufficiently elastic it is sure to develop cracks, when, of course, the negative will be spoiled. While possessing the necessary hardness, elasticity, and adhesiveness, it must permit at the same time of the plate being re-touched after being varnished. All the proportions are strictly by weight, whether of liquids or of solids:—

TABLE CLXIV.—PHOTOGRAPHIC VARNISHES.

1.	Sandarach	16 parts.
	Oil of lavender	12 ,,
	Chloroform	2 ,,
	Rectified spirits of wine	80 ,,

Filter from any insoluble matter.

2. Leave shellac in a concentrated solution of carbonate of ammonia, then drain off the ammonia salt, and replace it by pure water (shellac 1 part, water 8 parts). The shellac will then dissolve.

3.	Shellac	2 parts.
	Sandarach	12 ,,
	Mastic	12 ,,
	Ether	150 ,,

After the solution is complete add 9 parts of benzole.

4. Digest 2 parts of dammar with 9 parts of acetone in a well-corked bottle in a warm place for a fortnight, shaking occasionally. Then decant from the insoluble residue. Several coats of this varnish will be required. This varnish also answers well for paper.

5.	Shellac	75 parts.
	Sandarach	10 ,,
	95 per cent spirits of wine	915 ,,
6.	Amber, fused	2 ,,
	Copal	2 ,,
	Benzol	4 ,,
	Rectified spirits of wine	30 ,,
7.	Amber, fused	4 ,,
	Copal	4 ,,
	Mastic	2 ,,
	Petroleum ether	20 ,,
	Rectified spirits of wine	40 ,,
8.	Sandarach	40 ,,
	Turpentine, Venice	4 ,,
	Oil of lavender	5 ,,
	[illegible]	5 ,,

Spirit Varnishes for Rendering Linseed Oil Siccative.—No. 1.—Heat 6 parts of soft copal (powdered) in a mixture of 1 part ether and 6 parts of alcohol, and, when dissolved, add 4 parts of oil of turpentine.

No. 2.—Dissolve 1 part of copal (powdered) in 3 parts of ether, in which ½ part of camphor has been dissolved.

No. 3.—Digest 2 parts of elemi, 10 parts of mastic, 10 parts of sandarach, 3 parts of Venice turpentine, in 100 parts of spirits of wine or methylated spirit.

No. 4.—Dissolve 4 parts of rosin, 1 part of elemi in 12 parts of methylated spirit of wine.

No. 5.—Dissolve 5 parts of rosin and 1 part of mastic in 30 parts of methylated spirit.

No. 6.—Dissolve 1 part of camphor in 40 parts of methylated spirit, and then add 1 part of mastic and 2½ parts of sandarach.

No. 7.—Dissolve 5 parts mastic, 6 parts of sandarach, ¾ part Venice turpentine in 30 parts methylated spirit.

No. 8.—Dissolve 5 parts mastic, 10 parts sandarach resin, ½ part of Venice turpentine in 26 parts of spirits of wine.

When these spirituous solutions of resins are complete they are ready for use in the proportion of 5 to 10 per cent of oil to be rendered siccative (bulk or liquid measure). In preparing the above resinous solutions, all parts are taken by weight.

These oil siccative recipes are reproduced without prejudice for what they are worth. The writer has not tested their efficacy. The oils so treated may be useful with inert pigments, but they would cause lead, etc., pigments to set.

TABLE CLXV.—SPIRIT VARNISHES, COMPILED BY AN ITALIAN AUTHORITY.

	Alcohol, 96 per cent.	Sandarach.	Mastic.	Venetian Turpentine.	Amber.	Ground Glass.	Shellac.	Benzoin.	Sandal-wood.	Liver Shellac.	Elemi.	Anime.	Camphor.	Rosin.
1.	500	250	—	—	—	—	—	—	—	—	—	—	—	—
2.	1875	875	250	16	—	—	—	—	—	—	—	—	—	—
3.	2000	125	60	80	125	80	—	—	—	—	—	—	—	—
4.	8000	500	—	60	—	—	250	—	—	—	—	—	—	—
5.	1000	90	175	90	—	—	—	—	—	—	—	—	—	—
6.	1000	15	15	—	—	—	110	180	—	—	—	—	—	—
1.	5000	—	—	—	—	—	—	—	800 (1)	500	—	—	—	—
2.	1500	180	125	250	—	—	—	—	—	—	—	—	—	—
3.	1000	187	—	—	—	125	—	—	—	—	125	82	16	—
4.	1000	187	—	125	—	125	62	—	—	—	—	—	—	125
5.	4000	750	—	—	—	—	—	—	—	—	—	250	60	250
6.	1000	120	875	85	—	—	—	—	—	—	—	—	—	—
7.	2000	125	81	62	—	125	—	81	—	62	—	—	—	—
8.	4000	500	—	—	—	—	500	—	—	—	—	—	—	250
9.	1250	—	—	—	250	—	—	—	—	—	—	—	11	—
10.	1000	150	100	—	—	—	—	—	—	—	—	—	80	—
11.	875	575	—	180 (2)	—	—	90	—	—	—	—	—	—	180

Nos. 1 to 6 are spirit varnishes for general use. Nos. 1 to 4 are mahogany varnishes. Nos. 5 and 6 are flexible varnishes. No. 7 is for colour printing. Nos. 9 and 10 for metals.

TABLE CLXVI.—CONTINUATION OF TABLE CLXV.

Varnish.	Alcohol, 67 O.P.	Sandarach.	Mastic.	Shellac.	Copal.	Amber.	Anime.	Elemi.	Frankincense.	Dragon's Blood.	Venice Turpentine.	Lampblack.	Turmeric.	Gamboge.	Aloes.	Saffron.	Ground Glass.
Furniture .	9·6	500	360	—	120	120	250	—	250	—	—	—	—	—	—	—	—
Sculpture .	2000	400	—	100	—	—	—	—	—	500	100	—	—	—	—	—	—
Golden .	500	—	250	60	—	—	—	—	—	15	—	—	15	15	15	—	—
Physical Instrument	1000	100	—	50	—	—	—	100	—	50	—	—	35	81	—	10	140
Black .	4000	—	—	1500	—	—	—	—	—	—	180	45	—	—	—	—	—
For iron .	1125	—	—	180	—	60	—	—	—	—	—	—	60	—	—	—	—

Violin Varnish.—The golden-yellow varnish which violin makers used in the eighteenth century is given thus in an old work dated 1790: "Pound separately 4 oz. of stick lac, 4 oz. of gamboge, 4 oz. of dragon's blood, 4 oz. of annotta, and 1 oz. of saffron; put each separately into a quart of alcohol, and expose them for five days in a narrow-mouthed bottle to the sun, or in a very warm room, shaking them frequently. When all are melted (dissolved) mix them together."

Another "violin varnish" of the eighteenth century was made as follows: "Put 4 oz. of gum sandarach, 2 oz. of gum mastic, 1 oz. of gum elemi, into a quart of alcohol, and hang them over a slow fire till they are dissolved; then add 2 oz. of turpentine". By "turpentine" is probably meant Venice turpentine; but it may mean also spirits of turpentine.

Watin's formula for violin varnish was as follows:—

A.

Sandarach	125 parts by wt.
Seed lac	62 ,,
Mastic in tears	62 ,,
Elemi	31 ,,
Venice turpentine	62 ,,
Alcohol	1000 ,,

It will be seen that this formula is not sufficiently elastic. Another one, proposed as a substitute, was as follows:—

B.

Sandarach	80 parts by wt.
Mastic	100 ,,
Elemi	30 ,,
Coloured essence	60 ,,
Castor oil	50 ,,
Alcohol	1000 ,,

Without going into all the details of his experiment, an authority has arrived at a formula which he considers in every way suitable and satisfactory for the intended purpose. It is composed of:—

C.

Mastic (tears)	10 parts by wt.
Dammar, soft white	5 ,,
Coloured turps	100 ,,
Raw linseed oil	5 ,,

It is made as follows: A layer of ground glass is placed in a wide-bottomed flask, then the 100 parts of the coloured turps, then the mastic, and the two left in contact together for several hours, with frequent shaking. The dammar is then added, which takes another twenty-four hours for solution. In winter each period will require to be extended to thirty hours. The oil is then added, and well incorporated with the varnish by frequent shaking. After standing for another fifteen hours in diffused daylight the whole is filtered through a cotton cloth. The varnish is greatly improved by keeping from six to eight months before use. The red colouring matters are sandalwood deep (Calliatour), dragon's blood; and gamboge for the yellow; mixtures of the three giving any desired tint.

A colourless violin varnish is obtained from the following recipe:—

D.

Mastic (tears)	20 parts by wt.
Dammar, white	10 ,,
Turps	100 ,,
Raw linseed oil	12 ,,

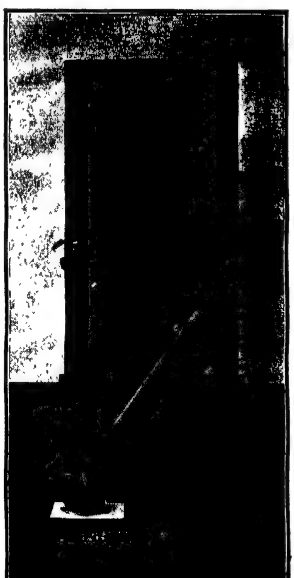


FIG. 54.—Filmometer. [See page 421.]

PART V.

TESTING AND ANALYSIS OF SPIRIT VARNISHES.

CHAPTER XXVI.

ANALYSIS, VALUATION, AND PRACTICAL TESTING OF SPIRIT VARNISHES—TECHNICAL VALUATION.

In the valuation of spirit varnishes, two great points must be carefully and minutely examined, viz. (1) the physical properties, and (2) the chemical composition. In examining the physical properties the chief points to be determined are the manner in which the varnish dries, and the time that elapses between the application and drying of the varnish. It is a *sine qua non* that the varnish should *not* dry tacky unless wanted as a mordant or fixture for gold-leaf or as a medium for applying colours in porcelain enamelling. The quicker the varnish dries, other things being equal, the more valuable and economical it is, as less time is lost by the workmen in waiting for a previous coat to dry before applying the next. The quickest and perhaps the best way to test the drying of a spirit varnish is to run some on to a glass slab and place it in a water-bath at 212° F. and note the time it takes to dry and the manner in which it dries, attacking the coat with the thumb-nail when the dry varnish is cool and pressing with all one's might the thumb on to the varnish to detect tackiness. Body, brilliancy, transparency, colour, elasticity, the hardness, as well as the capacity of the varnish to withstand wear and tear; the action of the weather and the alternations of temperature produced by day and night, summer and winter, etc., have each and all to be studied before a definite conclusion can be arrived at, having regard to the special object in view; the climate in which the varnish is to be used and the temperature or temperatures to which the object may be exposed during the whole course of its existence. A varnish, therefore, which may be very valuable for one purpose may be worthless, or worse than worthless, for another. The valuation of varnish, therefore, depends almost entirely upon the experience of the expert, and above all on his good sound commonsense. Through the long handling of varnish the true *bona-fide* expert can distinguish almost intuitively good varnish from bad. He calls to his aid the senses of sight, touch, and smell, and he knows how to apply each and all of these organs of senses so as to form

the best possible judgment on the quality of the varnish. Where it is a decided case for the thumb-nail and pressure of the thumb itself he does not apply a slight gliding motion of the fingers or a down hair-stroke motion of a single finger; where a bad judgment is formed or a test performed in a perfunctory way, a graph to illustrate such an error of judgment is highly misleading. The presence of Manila copal in spirit varnish may always be detected by its peculiar aromatic odour. The perception of this smell in a varnish at once recalls to the expert that Manila has a tendency to string on application. He therefore at once presses a drop between the finger and thumb, and if Manila be present after the spirit has evaporated to a certain extent the resin may be drawn out in long thong-like strings. It is, however, to be observed that certain other resins, e.g. common rosin, are often added to Manila copal to counteract this tendency.

Testing Varnish Films by the Filmometer.—The instrument consists essentially of a graduated upright tube seen on the left hand of the illustration (p. 419). This tube is fixed by means of sealing-wax to two circular brass plates between which the film to be tested is placed and which are clamped together while the test is being conducted. These plates are bored with a hole vertically under the orifice of the upright graduated tube. This hole measures exactly one square centimetre in area and is circular. The upright tube is graduated in lineal centimetres, and is called the pressure tube. The burette shown on the right of the illustration is also graduated in centimetres and contains mercury which is conveyed by the side limb of the pressure tube to the latter, and is the means by which pressure is brought to bear upon the film under test. Above the pressure tube is fixed a wheel over which runs a thread terminating at one end in a metal rod with a float at the end. The metal rod and float extend to near the bottom of the pressure tube. To the other end of the thread is attached a counterpoise. Immediately under the openings of the metallic plates are arranged two pieces of iron inclined at an angle of 90°, and insulated by a thin piece of india-rubber. These two plates are connected up by wires with a pair of electro magnets shown above the pressure tube, the circuit being completed through an electric bell shown behind the side limb of the pressure tube and switch shown in the centre of the diagram.

The film to be tested having been placed between the brass plates underneath the pressure tube, mercury is run into the pressure tube from the burette. As the mercury rises in the pressure tube it pushes the float upwards. When the weight of mercury in the pressure tube ruptures the paint film, the mercury falling on to the two insulated iron plates completes the electric circuit. The two small coils above the pressure tube instantaneously become magnetized and hold the metal rod firmly in position, thus enabling a reading to be taken of the height of the mercury accumulated in the pressure tube when rupture took place. At the moment when the coils become electrified the bell rings, and the operator who is carefully

watching the burette immediately turns off the stopcock and takes the reading on the burette.

Two readings are thus obtained : (1) the reading on the burette; (2) the reading on the pressure tube. The reading on the burette gives the weight of mercury necessary to rupture the film under the conditions of the experiment, while the difference between the readings of the burette and the pressure tube gives the volume due to the sag of the film which is taken as a measure of its elasticity. In the case of perfectly non-elastic substances the reading of the burette and the pressure tube would of course always bear the same relation.

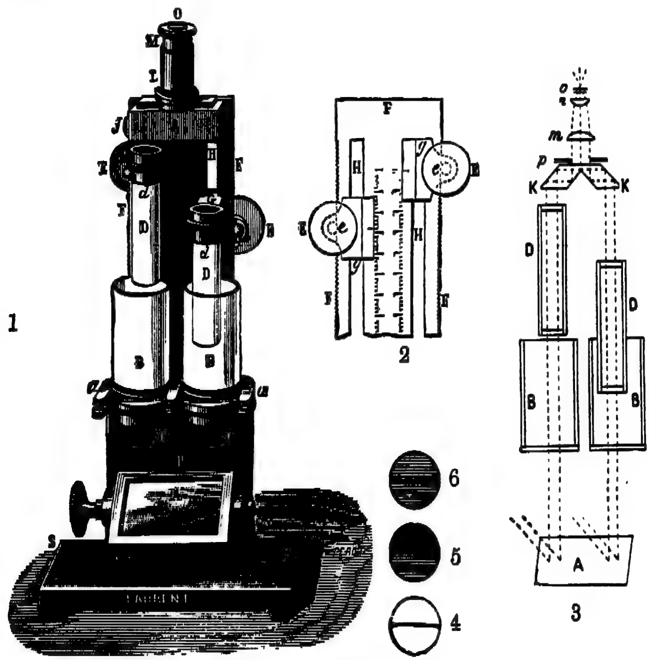


FIG. 55.—Duboscque's Colorimeter.

Temperature is a most important factor in film-testing experiments, and the experiments should be conducted at a uniform temperature. In America 70° F. is the temperature usually adopted. Here again an indifferent operator with an elaborate instrument of this nature may be constrained to give a less true opinion of a varnish film than a true expert with his thumb and thumb-nail as his only tools.

Colour.—One of the most important points connected with the valuation of varnishes is its colour at the outset and the amount of change in colour after the varnish is applied. According to Mr. Crace it is not always the palest varnishes that are most satisfactory in retaining their colour, cases sometimes occurring where a pale

varnish darkens so much on exposure as to become actually darker than one originally much deeper in colour after the two had been exposed under the same conditions for a year or two.

The comparative depth of colour of varnishes may be estimated by Duboscque's colorimeter.

Description.—Fig. 1 represents front view of apparatus. When in use the operator stands behind. Fig. 2 represents back view, and shows the divisions and the vernier. Fig. 3 the path of the light inside the instrument. Fig. 4 shows the appearance of the diaphragm seen through the eyepiece when the apparatus is regulated to zero. Fig. 5 shows the same and use as Fig. 6 when an equality of tones has been obtained.

The Path of the Light (Fig. 3).—The diffused light, a clamp or a monochromatic burner, after being reflected on to a mirror A, is separated into two beams, which penetrate respectively into the two tubes B, B. The right beam is reflected twice in the right half of prism K, penetrating into the eyepiece; it only affects the right half of the field; the left beam does exactly similar, affecting only the left side of the field. No bright light is needed; it is sometimes better to place before the mirror A a piece of ground glass. (A piece is supplied.)

Instructions for Using.—This instrument gives relative results. Place standard coloured liquid in left tube B. Place liquid to be compared in right tube B. Now lower the right tube D until it reaches what appears to be the most convenient point for estimation, which depends on the colour of the liquids; now note the divisions on scale corresponding to the standard liquid. Lower the tubes D till they touch the bottom of B and the verniers *g* mark zero. Look through O, and then gradually move the apparatus till both half fields are equally illuminated; now move screws E till equality of tone is produced. For two liquids the colour is inversely proportional to the density of the column of liquid traversed by the light and proportional to the quantity of dissolved matter.

Example.—Suppose a liquid gives a reading of $12^{m}5$, and the standard is 10^{m}, we shall then have the following proportion:—

$$\frac{\text{Colour of liquid}}{\text{Colour of standard}} = \frac{\text{height of standard}}{\text{height of liquid}} = \frac{10^{m}}{12^{m}5} = 0{\cdot}8,$$

so the colour of the standard being represented by 1, that of the liquid will be 0·8.

To Clear Tubes B.—Raise pistons D, take out tube B, unscrew ring C, take off the glass at bottom. The rest can be easily cleaned by means of a fine cloth.

Viscosity of a Spirit Varnish and What it Teaches.—Rosin is the least viscous of all resins, especially when heated. When the viscosity of a warm spirit varnish is very low compared with its density, then it may be taken that it contains much rosin or oleo-resin.

Description of the Apparatus.—The instrument consists of a

silvered brass oil-cylinder, furnished with an agate jet, and surrounded by a copper-bath. A copper tube, closed at the lower end, projecting at an angle of 45° from the side of the bath, near the bottom, provides a means of heating the bath liquid, and by the use of a revolving agitator, which forms part of the apparatus, the heated liquid rising from the copper tube can be uniformly distributed through the bath. The agitator carries a thermometer to indicate the temperature of the bath. The container is furnished with a stopper, consisting of a small brass sphere attached to a wire, the sphere

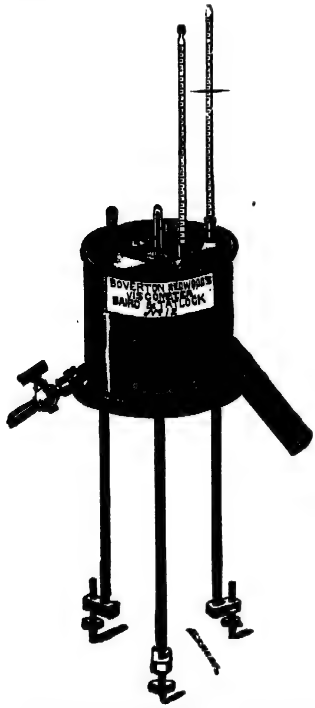


Fig. 56.—Viscometer. General view.

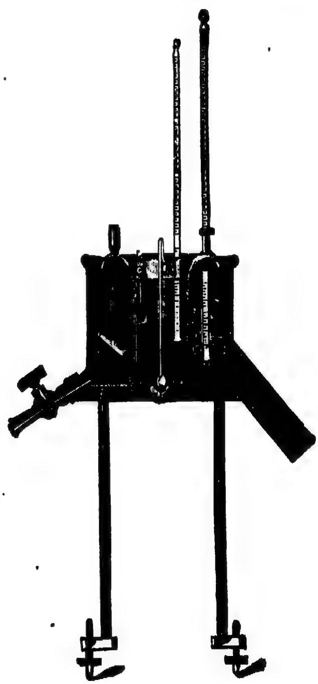


Fig. 57.—Viscometer. Section.

resting in a hemispherical cavity in the agate jet. A short standard, attached to the container, carries a clip to support a thermometer in the varnish. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket, terminating in an upturned point, which forms a gauge of the height of the oil level. The instrument is supported on a tripod stand provided with levelling screws.

Directions for Use.—The bath is filled with a suitable liquid to a height roughly corresponding with the point of the gauge in the container. Water answers well for the temperature up to 200° F., and for higher temperatures a heavy mineral oil may be used. The

liquid having been brought to the required temperature, the varnish to be tested, previously brought to the same temperature, is poured into the oil-cylinder, until the level of the liquid just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the varnish. The ball valve is then raised, a stop-watch at the same time started, and the number of seconds occupied in the outflow of 50 c.c. noted. It is of the greatest importance that the container should be filled exactly to the point of the gauge, after inserting the thermometer, and that the given temperature should be precisely maintained during the experiment, a difference of $\frac{1}{2}^{\circ}$ F. making an appreciable alteration in the viscosity of some oils. It is also essential that the varnish should be quite free from dirt or other suspended matter, and from globules of water, as the jet may be otherwise partially obstructed. If the container requires to be wiped out, paper rather than cloth should be employed, as filaments of the latter may be left adhering. When varnishes are being tested at temperatures much above that of the laboratory, a gas flame is applied to the copper heating tube, and the agitator kept in gentle motion throughout the experiment.

NOTE.—The jet should be carefully examined before the apparatus is used, and, if necessary, should be cleaned by passing a piece of soft string through it. The apparatus should be adjusted by means of the levelling screws, so that a spirit level placed on the top of the varnish-cup shows it to be horizontal.

Method of Expressing the Results.—Sir Boverton Redwood recommends that the number of seconds occupied in the outflow of 50 c.c. of the fluid under examination should be multiplied by 100 and divided by 535 (the number of seconds occupied in the outflow of 50 c.c. of average refined rape oil at 60° F.). The resulting figures should then be multiplied by the specific gravity of the fluid under examination at the temperature of the experiment, and divided by 915 (the specific gravity of refined rape oil at 60° F.); the necessary correction for specific gravity being thus made, the final figures will express the viscosity of the varnish, at the temperature of the test, in terms of viscosity of refined rape oil at 60° F.

The Flash-point of Spirit Varnishes as a Key to the Solvent Present.—The apparatus for determining the flash-point of volatile liquids like spirit varnish consists of a vessel, the outlines of the essential portion of which are shown on the top of the illustration (Fig. 58). The main bulk of the large cylinder is filled with water, but the cup containing the oil dips into a hot air chamber, heated by the cylindrical bath underneath. The test apparatus should be placed for use in a position where it is not exposed to currents of air or draughts. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing

hot or cold water in the bath, or in a vessel from which the bath is

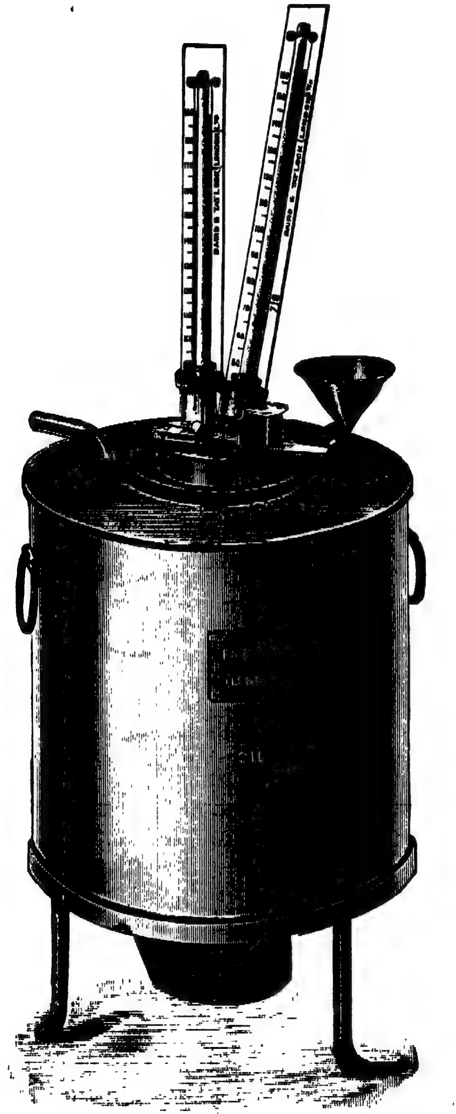


FIG. 58.—Abel's Flash-point Apparatus.

filled, until the thermometer, which is provided for testing the temperature of the bath, gives the proper indication, or by heating the

water with the spirit lamp which is attached to the stand of the apparatus until the required temperature is indicated. If the water has been heated too highly it is easily reduced to 130° F. by pouring in cold water to replace a little portion of the warm water, until the thermometer gives the proper reading. When a test has been completed this water-bath is again raised to 130° F. by placing the lamp underneath, and the result is readily obtained whilst the petroleum cup is being emptied, cooled, and refilled with a fresh supply to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with. The test lamp is prepared for use by fitting it with a piece of flat plaited candle wick, and filling it up with colza or rape oil up to the lower edge of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 inch in diameter, and this size of flame is maintained by simple manipulation from time to time with a small wire trimmer. When gas is available it may be conveniently used instead of the little oil lamp, and for this purpose a test flame arrangement for use with gas has been devised. The bath being raised to the proper temperature the liquid to be tested is introduced into the cup, being poured in slowly, until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed, and if it exceeds 65° F. the samples to be tested should be cooled down (to about 60° F.) by immersing the bottle containing them in cold water, or by any other convenient method. The lid of the cup with the side closed is then put on and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in a proper position the scale of the thermometer faces the operator. The test lamp is then placed on position upon the lid of the cup. The lead line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the cup containing the liquid to be tested is watched. When the temperature has reached about 66° F. the operation of testing is commenced, the test flame being applied once for every rise of one degree in the following manner: The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation. *Note.*—If it be desired to employ the test apparatus to determine the flash-points of very low volatility, the mode of proceeding is to be modified as follows: The air chamber surrounding the cup is to be filled with cold water to a depth of 1½ inches, and the heating vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus and kept there during the entire operation. With a liquid with a flash-point of 150° F. the operation may be commenced with water previously heated to 120° F.,

instead of with cold water. The above apparatus (Abel's) is the only legal one. It is useless for railway or other purposes to work with another. Results obtained by instruments other than the legally recognized one, or its authorized modification for compositions (Figs. 61-2), will not be accepted in a court of law; but as Gray's apparatus (Fig. 59) gives highly useful indications in cases where

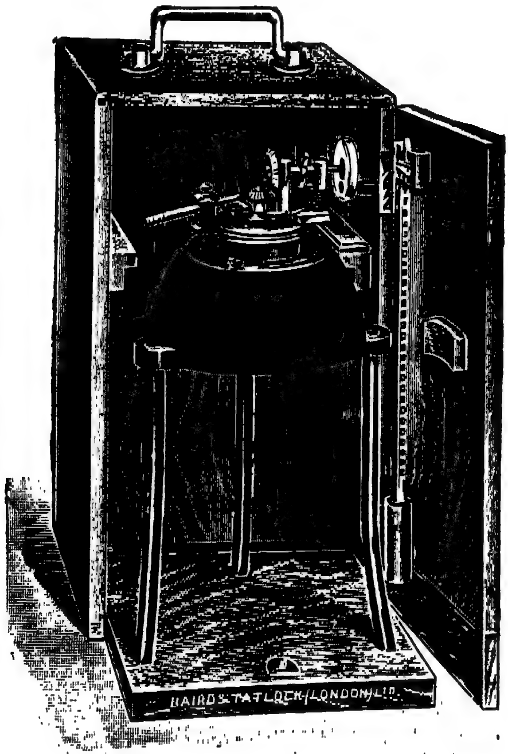


FIG. 59.—Gray's Flash-point Apparatus. General view.

domestic legislation plays no part, we reproduce a section of it here (Fig. 60). It will be seen that it is fitted with a stirrer, otherwise it shows the nature of the cup inside the Abel's, and it also shows the jet which dips automatically into the oil cup by a mechanical arrangement. Gray's apparatus and its *modus operandi* are fully described in Livache and McIntosh's "Varnishes," Vol. I, but the present illustrations show a new and improved form of this instrument.

The reason for taking the atmospheric pressure is because the

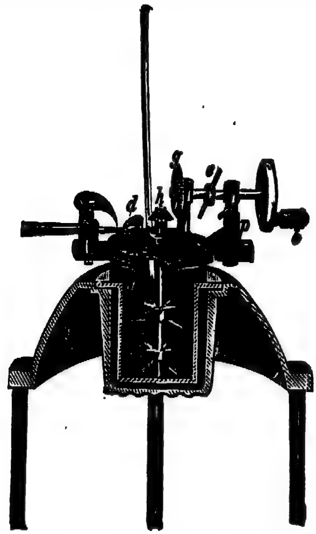


FIG. 60.—Gray's Flash-point Apparatus. Section.

flash-point varies to a considerable extent with the pressure, as shown in the following table:—

TABLE CLXVII.—FLASH-POINT CORRECTION TABLE FOR VARIATIONS IN ATMOSPHERIC PRESSURE.

Atmos. Press. in mm.	Flash-points in °C.												
685	16·4	16·9	17·4	17·9	18·4	18·9	19·4	19·9	20·4	20·9	21·4	21·9	22·4
690	16·6	17·1	17·6	18·1	18·6	19·1	19·6	20·1	20·6	21·1	21·6	22·1	22·6
695	16·7	17·2	17·7	18·2	18·7	19·2	19·7	20·2	20·7	21·2	21·7	22·2	22·7
700	16·9	17·4	17·9	18·4	18·9	19·4	19·9	20·4	20·9	21·4	21·9	22·4	22·9
705	17·1	17·6	18·1	18·6	19·1	19·6	20·1	20·6	21·1	21·6	22·1	22·6	23·1
710	17·3	17·8	18·3	18·8	19·3	19·8	20·3	20·8	21·3	21·8	22·3	22·8	23·3
715	17·4	17·9	18·4	18·9	19·4	19·9	20·4	20·9	21·4	21·9	22·4	22·9	23·4
720	17·6	18·1	18·6	19·1	19·6	20·1	20·6	21·1	21·6	22·1	22·6	23·1	23·6
725	17·8	18·3	18·8	19·3	19·8	20·3	20·8	21·3	21·8	22·3	22·8	23·3	23·8
730	18·0	18·5	19·0	19·5	20·0	20·5	21 0	21·5	22·0	22·5	23·0	23·5	24·0
735	18·1	18·6	19·1	19·6	20·1	20·6	21·1	21·6	22·1	22·6	23·1	23·6	24·1
740	18·3	18·8	19·3	19·8	20·3	20·8	21·3	21·8	22·3	22·8	23·3	23·8	24·3
745	18·5	19·0	19·5	20·0	20·5	21·0	21·5	22·0	22·5	23·0	23·5	24·0	24·5
750	18·7	19·2	19·7	20·2	20·7	21·2	21·7	22·0	22·7	23·2	23·7	24·2	24·7
755	18·8	19·3	19·8	20·3	20·8	21·3	21·8	22·3	22·8	23·3	23·8	24·3	24·8
[1] 760	19·0	19·5	20·0	20·5	21·0	21·5	22·0	22·5	23·0	23·5	24·0	24·5	25·0
765	19·2	19·7	20·2	20·7	21·2	21·7	22·2	22·7	23·2	23·7	24·2	24·7	25·2
770	19·4	19·9	20·4	20·9	21·4	21·9	22·4	22·9	23·4	23·9	24·4	24·9	25·4
775	19·5	20·0	20·5	21·0	21·5	22·0	22·5	23·0	23·5	24·0	24·5	25·0	25·5
780	19·7	20·2	20·7	22·2	21·7	22·2	22·7	23·2	23·7	24·2	24·7	25·2	25·7
785	19·9	20·4	20·9	21·4	21·9	22·4	22·9	23·4	23·9	24·4	24·9	25·4	25·9

[1] Normal pressure.

Explanation.—A liquid flashing at 16·4° C. at 685 mm. pressure would flash at 19° C. at the normal pressure of 760 mm., and so on.

TABLE CLXVIII.—SHOWING FLASH-POINTS IN °C. OF VARIOUS LIQUIDS.

	°C.		°C.
Acetic acid glacial	44	Motorbenzol	90
Alcohol, 94-5 per cent	14-20	Olive oil	215-60
Aniline	26	Paraffin (? wax)	158-195
Benzene (coal-tar)	– 15	„ oils	107
Brandy	29	Petroleum ether	– 20
Camphor oils	55	„	21-23
Carbon disulphide	– 20	Poppy oil	255
Cotton-seed oil	170	Rape „	210-305
Dimethylaniline	76	Rosin „	130
Engine oil spindle	135-190	Sesame oil	255
Ether	– 20	Sherry	54
Fusel oil	46-54	Sludge (petroleum refinery)	40
Hollands gin	32	Solar oil	60
Kaiser oil	40-48	Spermaceti	250
Kerosene	27-33	Tar	48
Lard oil	240	Toluene	7
Linseed oil	316-350	Toluidine	85
Lubricating oil	260-320	Turpentine spirits	35
„ „ light motors	200	Whisky	28
Methyl alcohol	– 0	Xylene	30
Monochlorbenzol	27-5	Xylidin	97

In working with the Abel Pensky instrument the temperature (t) at which the test is first applied varies with the atmospheric pressure (b), as shown in the following table:—

TABLE CLXIX.—ABEL PENSKY FLASH-POINT AND PRESSURE.

b.	t.	b.	t.
685-695 mm.	+ 14°	735-745 mm.	+ 16·0°
695-705 „	14·5°	745-755 „	16·5°
705-715 „	15·0°	755-765 „	17·0°
715-725 „	15·5°	765-775 „	17·0°
725-735 „	16·0°	775-785 „	17·5°

Directions for Testing the Flash-point of Petroleum Mixtures such as Spirit Varnish Enamels.—1. *Liquid Mixtures.*—Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the manner set forth in Schedule 1 to the Petroleum Act, 1879 (see pp. 425-7).

2. *Viscous and Sedimentary Mixtures.*—Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner set forth in Schedule 1 to the

TABLE CLXX.—SHOWING THE FLASH-POINT OF METHYL, ETHYL, AMYL, AND OTHER ALCOHOLS OF VARIOUS PERCENTAGE STRENGTHS.

	100 per cent. °C.	80 per cent. °C.	60 per cent. °C.	40 per cent. °C.	20 per cent. °C.	10 per cent. °C.	7½ per cent. °C.	5 per cent. °C.	4 per cent. °C.	2 per cent. °C.
Methyl alcohol	9·5	16·75	22·75	30·0	44·25	58·75	65·25	—	—	—
Ethyl ,, ...	12·0	19·0	22·75	26·25	36·75	49·0	—	62·0	68·0	—
Propyl ,, (primary)	23·0	29·5	31·25	32·0	33·75	41·0	46·0	52·25	56·0	—
Propyl ,, (secondary) . . .	11·75	17·25	19·25	20·25	28·75	39·25	—	—	—	—
Butyl ,, normal (primary) . .	35·0	40·25	41·0	41·5	41·25	—	42·75	—	—	55·0
Isobutyl ,, ...	27·5	33·75	33·75	33·75	34·75	—	36·0	44·25	—	52·25
Butyl ,, (tertiary)	11·5	15·25	16·25	16·0	—	30·25	—	41·5	—	—
Isoamyl ,, (primary)	12·0	—	—	—	—	—	—	—	—	—
Amyl ,, (tertiary)	19·5	26·25	—	—	—	29·25	—	37·5	—	—
Allyl ,, ...	21·5	27·5	29·25	30	33·0	41·75	—	54·5	—	—

Petroleum Act, 1879. In carrying out such separation, care must be taken to minimize the evaporation of the petroleum. The separation of the sediment must not be effected by distillation. Where the petroleum mixture is such that sediment cannot be separated by the aforementioned means, or where it is of a viscous nature, as in the

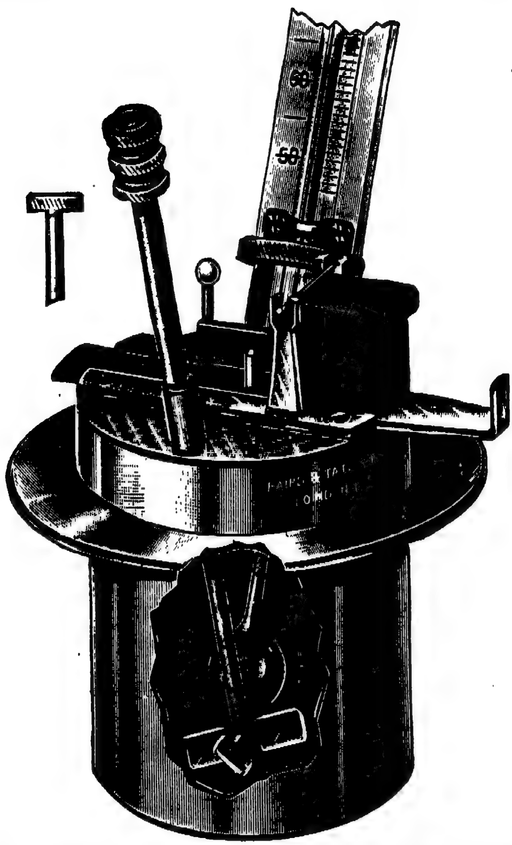


FIG. 61.—Government Flash-point Apparatus for viscous and sedimentary mixtures (varnishes, paints, enamels, antifouling compositions, polishing pastes), showing internal arrangements of cup.

case of india-rubber solution, quick-drying paints, etc., such mixture shall be tested in the apparatus modified as shown in the drawing hereto. This apparatus differs from that prescribed in Schedule 1 to the Petroleum Act, 1879, only in the addition of a stirrer to equalize the temperature throughout the sample under test. In carrying out the test of a viscous petroleum mixture, this stirrer shall be constantly revolved at a slow speed, except when applying the test

flame, with the fingers, the direction of revolution being that of the

FIG. 62.—Government Flash-point Apparatus for viscous and sedimentary mixtures (varnishes, paints, enamels, antifouling compositions, polishing pastes), fitted up for applying test.

hand of a clock. With the exception of the use of the stirrer, the manner of carrying out the test shall be that set forth in Schedule 1

to the Petroleum Act, 1879. The stirrer may be removed by grasping the spindle just above the blades with the finger and thumb, and unscrewing the upper sheath. The opening in the lid, through which the stirrer passes, may then be closed by a plug provided for the purpose. When this has been done, the apparatus shall be deemed to comply with the specification set forth in Schedule 1 of the Petroleum Act, 1879, and may be used for testing ordinary petroleum or solid petroleum mixtures. A model of the aforementioned apparatus will be deposited with the Board of Trade, and the provisions of Section 3 of the Petroleum Act, 1879, in regard to verification and stamping shall apply also to such apparatus as though it were the apparatus prescribed by the said Act. For the purpose of carrying out such verification the stirrer shall be removed and the opening plugged as hereinbefore directed. The apparatus shall then be tested with ordinary petroleum. The stirrer shall be verified by comparison of measurements.

3. *Solid Petroleum Mixtures.*—Where the petroleum mixture is solid, as in the case of naphtha soaps, etc., the apparatus to be used for the test shall be that prescribed in Schedule 1 of the Petroleum Act, 1879. The method of carrying out the test of such solid mixture shall be as follows: The solid mixture must be cut into cylinders 1½ inches long and ¼ inch in diameter by means of a cork borer or other cylindrical cutter having the correct internal diameter. These cylinders are to be placed in the petroleum cup of the testing apparatus in a vertical position in such number as will completely fill the cup. The cylinders must be in contact with one another, but must not be so tightly packed as to be deformed in shape. Five or six of the cylinders in the centre of the cup must be shortened to ½ inch to allow space for the thermometer bulb. The air-bath of the testing apparatus must be filled to a depth of 1½ inches with water. The water-bath must then be raised to and maintained at a temperature about 75° F. The cup must then be placed in the air-bath, and the temperature of the sample must be allowed to rise until the thermometer in the oil cup shows 72° F., when the test flame must be applied. If no flash is obtained, this temperature must be maintained constant in the oil cup for one hour, at the expiration of which time the test flame must again be applied. If a flash is obtained, the solid mixture will be subject to the provisions of the Petroleum Acts in virtue of this Order.

NOTE.—It may in many cases save time in testing samples of petroleum mixtures to apply the test flame after the sample has been a few minutes in the cup, and while still at the temperature of the room in which the test is being carried out, provided that this temperature is below 73° F. If a flash is obtained by this means, it is unnecessary to proceed with the test at a higher temperature.

Chemical Analysis of Spirit Varnish.—From the chemical point of view the analysis of varnish consists in the determination of the solvent or solvents and the resin or resins (natural or artificial) and

their relative proportions, that is, of the solvents when more than one is present, to each other, and also of the different resins or other soluble solid bodies to each other and the relative aggregate proportion of the liquids to the aggregate of the solids, and should be so expressed as to constitute a formula from which the intelligent varnish-maker may match any sample of varnish submitted to him and thus enable him to quote a price or submit a tender for the supply of the same in large or small quantities. But the buyer of varnish or the tenderer offering to supply same according to a certain formula or analysis must beware of the radical difference in the meaning of so many lb. of say shellac to a gallon, and so many lb. in a gallon. So many lb. of resin in a gallon mean that so many lb. of resin or resins are to be taken and dissolved in the solvent so as to make the varnish when finished measure one gallon. There cannot therefore be a gallon of solvent in the finished varnish. This of course is fundamentally different from taking so many lb. of resin and dissolving the same in a gallon of alcohol, when the bulk of the alcohol will be increased by the bulk of the resin, the latter occupying almost the same bulk in a spirit solution as it does in its separate existence.

The Density or Specific Gravity of a Varnish, its Mode of Determination and the Lesson it Conveys.—As to the method of taking the specific gravity of a spirit varnish, take a bottle of a capacity of 1000 grain measures of distilled water up to mark at 60° F., tare it or counterpoise it, fill up to mark with the varnish at 60° F., insert stopper with hole drilled through it and wipe well, getting quit of air bells; place on weighing pan of balance and counterpoise on other pan. The actual number of grains in integers required to restore equilibrium gives the specific gravity of the varnish to the third decimal place, water = 1·0. The density of a spirit varnish can very well be taken by means of a hydrometer marking say 0·850 to 0·900, which can be got from any dealer in chemical apparatus for about 1s. 6d. (Fig. 23, Vol. I), and anyone of discrimination can find numerous other uses for this instrument both in the buying and testing of solvents and in the testing of spirit varnishes. Any deviation from the usual specific gravity of a spirit varnish means some alteration in the making whether for good or evil. The point to be borne in mind is that varnish-makers of good reputation always make their varnishes from the same raw materials and in the same proportions. The specific gravity of their varnish should not alter; if it does the buyer has a right to know the reason why; if the specific gravity increases the question is whether a cheaper resin, such as common rosin, has not been introduced and a larger amount of resins brought into solution per gallon in order to make up for the diminution of the viscosity caused by the introduction of rosin. There are no end to the questions which the hydrometer will answer. When judiciously questioned, it may even point out that weaker alcohol is being used if the specific gravity of the varnish has increased, other factors remaining constant.

The great enlightenment which three useful tools—a Westphal balance (an elaborate hydrometer), a graduated measure, and a viscometer—give on spirit varnish-making is well shown in the following table specially prepared for this treatise.

TABLE CLXXI.—Showing—as the result of direct experiments (under the direction of Mr. Chas. Harrison) by F. A. Flack, at the Borough Polytechnic, Session 1904-5, Oil and Colour Trade Class—the increase in (*a*) density, (*b*) volume, and (*c*) viscosity of solutions of American Water White Rosin, from 0·1 lb. dissolved in one British Imperial gallon of methylated spirit up to 5 lb. per gallon.[1]

Lb. of Rosin per gal. of Methylated Spirit, 61 O.P., 0·827 at 60° F.	Density of Solution (Westphal Balance) at 60° F., Water = 1·00.	Increase of Volume per cent.	Viscosity 50 c.c. in seconds of time at 70° F., Redwood's Viscometer.	Lb. of Rosin per gal. of Methylated Spirit, 61 O.P., 0·827 at 60° F.	Density of Solution (Westphal Balance) at 60° F., Water = 1·00.	Increase in Volume per cent.	Viscosity 50 c.c. in seconds of time at 70° F., Redwood's Viscometer.
0·1	0·8295	—	20	2·6	0·877	22·0	39
0·2	0·8296	0·4	20	2·7	0·878	22·4	40
0·3	0·832	1·0	20	2·8	0·880	23·6	41
0·4	0·8346	1·86	21	2·9	0·882	24·0	41
0·5	0·8357	2·8	22	3·0	0·884	27·2	42
0·6	0·8369	3·8	23	3·1	0·886	28·6	42
0·7	0·839	4·46	24	3·2	0·887	30	43
0·8	0·842	5·8	24	3·3	0·889	30·4	44
0·9	0·845	6·4	24	3·4	0·890	31·6	44
1·0	0·847	8·6	25	3·5	0·892	32	45
1·1	0·849	9·8	26	3·6	0·893	32·6	45
1·2	0·851	11·2	28	3·7	0·895	33·2	47
1·3	0·853	12·0	28	3·8	0·896	34·4	47
1·4	0·855	13·2	29	3·9	0·897	35·0	48
1·5	0·857	14·6	29	4·0	0·898	35·8	49
1·6	0·859	15·6	30	4·1	0·898	36·4	50
1·7	0·861	16·6	30	4·2	0·899	37·2	52
1·8	0·863	17·8	31	4·3	0·901	38·0	54
1·9	0·865	18·6	32	4·4	0·903	40·6	56
2·0	0·867	19·8	33	4·5	0·905	41·2	57
2·1	0·869	20·2	34	4·6	0·906	42·0	60
2·2	0·871	20·6	35	4·7	0·907	43·2	63
2·3	0·873	21·0	37	4·8	0·907	44·0	65
2·4	0·874	21·2	37	4·9	0·908	44·6	66
2·5	0·876	21·8	38	5·0	0·909	46·6	67

N.B.—This table agrees remarkably well with theory. Thus 10 lb. of dry rosin in one single fused lump occupy, roughly, the cubical space of $\frac{10}{11}$ of a gallon (possibly $\frac{100}{108}$ would be nearer, but let us take $\frac{10}{11}$ for simplicity's sake); therefore 5 lb. will equal $\frac{5}{11}$ of a gallon, or 0·454 gallon. Rosin thus displaces its own bulk of methylated spirit when dissolved therein. Shellac swells the bulk of methylated spirit to practically the same extent as rosin, but it increases the viscosity in a much more decided degree. Similar figures as to the density of shellac solutions are still wanting, and should give valuable assistance. The deductions made from the hydrometer indications can, if need be, be controlled by distilling off the solvent and weighing the residue.

[1] American readers will please remember that a British Imperial gallon of water weighs 10 lb.

The Acid Reaction of Spirit Varnishes and Oil Varnishes.—Varnish resins in solution react acid, and even if the drying oils used in oil varnishes react neutral when fresh, the latter always react acid as apart from the acid nature of the raw resins. The drying oils, even if neutral when used, become acid on heating. Heat liberates acids akin to acetic acid from varnish resins and sets free fatty acids from even neutral linseed oil. If we add to that the fact that spirits of turpentine unless newly rectified is always more or less acid, it will be readily seen that oil varnishes contain ingredients which speedily attack such a sensitive metal as copper. Even if we render linseed oil perfectly neutral by boiling with an alkaline solution, the oil on drying again assumes an acid reaction. So as to produce oil varnishes without copal, dammar, and amber, varnishes from various sources were treated with both hot and cold alkaline lye, but the neutral action so obtained reverted to an acid one on drying. It is thus impossible to produce oil varnishes to dry neutral; even *ester* varnishes react acid on drying, and *ester* resins exhibit no acid reaction. Absorption of oxygen and an acid reaction will always occur on the drying of oil varnishes made from any varnish resin, linseed oil, and spirits of turpentine, while the same resins, if dissolved in turpentine oil or any other volatile solvent, do not undergo any change in their characteristics during the drying process.

This acid reaction of oil varnishes has no effect on varnished work on wood, iron, canvas, etc.; it only shows itself with certain pigments, which are ground in the varnishes, as either a complete elimination of the pigment, or a jellifying called livering is the result. Characteristic is zinc white, which does not agree with all copal varnishes nor with spirit varnishes, while it can be readily ground together with raw linseed oil, boiled oil, dammar varnish (even in combination with boiled oil and oil of turpentine), and will keep permanently without decomposition.

But it is an open question how the dried coatings made with oil varnishes behave on easily oxidizable metals or alloys. Some military authorities assert that spirituous varnishes, even in a perfectly hard dry layer, cause a weak, scarcely noticeable reaction upon sheet brass, and varnishes used for the varnishing of cartridge caps must show no acid reaction during the work, nor must any effects be noticeable after drying. If a piece of tin coated with a spirit varnish not perfectly free from acid is placed in a dry state upon polished brass the bad effects are to be distinctly seen on the borders of the spots so covered. So sensitive is brass to the action of a varnish not free from acidity that the varnish itself will become green after two or three brass cartridge caps are varnished, that is to say, the brush used to coat the caps will convey to the varnish enough dissolved resinate of copper to colour the liquid varnish in a small bottle green. The brass tap of a filter took a green cast after a spirit varnish had been on the brass for but a few minutes. This green coloration is most distinct when a spirit varnish is used as a vehicle for bronze powder.

If the mixture is allowed to stand for a few hours in a small bottle a very decided green coloration soon manifests itself. A solid piece of metal, such as a copper coin, only causes a change in the colour after some weeks.

In marked contradistinction to oil varnishes and even to boiled oil itself, with both of which an acid reaction always occurson drying, spirit varnishes can be easily manufactured free from acid by several well-known processes which consist in treating the resins with caustic or carbonated alkali. Dammar is the chief resin that is so treated. But the use of dammar varnish is limited owing to the brittle nature of the resin. Both shellac and sandarach may be made to produce acid-free varnishes by fusing either of them with anhydrous carbonated alkali for several hours and dissolving the pulverized fused mass in alcohol. (But oil of turpentine will, if added to such a solution, turn it green, in contact with bronze powder.) Undissolved copal and a few other resins cannot be rendered acid free. It is necessary to act on their solution by adding small quantities of alkaline fluid, say dilute alcoholic potash, which may also be done with both shellac and sandarach so as to avoid fusion. Spirit varnishes are applied to wood, leather, metal, irrespective of their acid reaction, for they are not known to attack the surface on which they are applied under ordinary circumstances, but in special cases, such as varnishing sensitive metals and vehicles for bronze powders, varnishes absolutely free from acid are required.

Testing the Action of Solutions of Resins on Colouring Principles. —As a rule, the lack of fastness of varnish stains and coloured lacquers has been ascribed to the colour, but Namias shows that the resin also comes into question. Coloured spirit varnishes are usually solutions of resins in methylated spirits to which spirit-soluble anilines have been added. For a few colours, especially yellow and orange, vegetable colours are substituted when a good fastness to light is required. For most commercial spirit varnishes, however, spirit-soluble anilines must be used to get the required vivacity of colour and variety of tint. Namias experimented on the following: For yellow, metanil yellow, auramine, picric acid, chrysoidine; for red, magenta, safranine, rhodamine; for blue, Victoria blue, saigon blue; for green, brilliant green, malachite green; for violet, methyl violet, spirit-soluble indazine; for black, spirit-soluble nigrosine. Of these picric acid and nigrosine alone resist light. The others fade more or less rapidly. In a series of experiments Namias noted that the action of the light on the colour is enormously increased by the presence of the resin, and that different resins do not exert this influence to the same extent. On exposing to the sunlight two plates, one with a coat of coloured varnish and the other with the same colour simply dissolved in spirits, he noted that when the varnish had completely lost its colour there was no perceptible change in the other coat. He next tried all the different resins ordinarily used for spirit varnishes, shellac, sandar-

ach, dammar, mastic, elemi, rosin, and myrrh. Of these, shellac and myrrh had the least effect in quickening the action of the light and elemi and mastic had the greatest effect. Sandarach, rosin, and dammar had a medium effect, which seemed to increase in the order in which they are written. It is possible that the influence of the resin is both chemical and physical. No doubt the decoloration is partly due to oxidation, as the decoloration is much retarded if the coats of colour are covered with a thin sheet of glass. It is possible that under the influence of air and light the resins give off ozone in different degrees. It is known that turpentine oxidizes in the air, giving off small quantities of ozone, and the same seems probable as concerns all resins exposed to air.

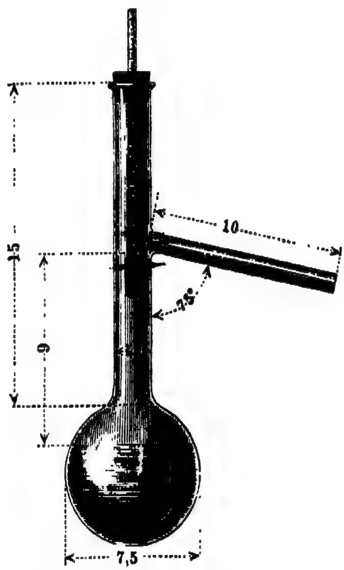


FIG. 63.—Fractional Distillation Flask of standard measurement, showing position of thermometer in determining boiling-point.

Detecting the Resin and Solvent by Smell.—The smell of the varnish gives a good indication of the solvent or solvents present and often of the resin. Methylated spirit has got a characteristic smell, wood-spirit another; coal-tar naphtha, petroleum spirit, amylic alcohol (fusel oil), amylic acetate (essence of pears), and in fact solvents in general have each got a highly characteristic odour. Even rectified rosin spirit has got a smell recalling peppermint. After endeavouring to recognize the solvent by the smell, the indications of the olfactory nerves are confirmed by the boiling-point. As to the smell of the resin in the varnish, that of benzoin is not masked even by the smell of methylated spirit.

The Boiling-point as a Key to the Solvent Present in a Spirit Var-

nish.—The boiling-point of volatile liquids like alcohol is quite as characteristic as the melting-point is in the case of solids. The apparatus used is a distillation flask (Fig. 63) into which the fluid is run. The cork is pierced by a hole through which the stem of a thermometer passes, and the flask is connected with a condenser. The vapours rise up the neck of the flask, and begin to condense on the sides of and on the thermometer. The mercurial column rises and remains stationary when the mercury and the glass of the stem are of the same temperature as the vapour. This temperature is noted and the atmospheric pressure at the time of the experiment. Absolute pure alcohol C_2H_5HO has a constant boiling-point, so also has pure benzol and solvents which are definite chemical compounds generally. Spirits of turpentine is not a perfectly pure well-defined body, but a mixture of different terpenes with closely similar boiling-points. When a mixture of two or more volatile substances like the terpenes in question is distilled, it begins to boil at some temperature lying between the boiling-point of the constituents. As the distillation of the spirits of turpentine goes on the boiling-point rises, till, towards the end of the operation, it is usually the same as that of the terpene which boils at the higher temperature. Before fractionally distilling spirits of turpentine, care should be taken to see that it is free from even traces of water, as a mixture of spirits of turpentine distils 2° or 3° C. below the boiling-point of water itself. Traces of water may be removed by shaking the turps with fused calcium chloride. For the reasons given above, the boiling-point of American spirits of turpentine is thus not constant, and a mixture of several solvents is highly erratic in its boiling-points. In quick-drying compositions, for instance, the solvent may consist of spirits of turpentine, gasolene, petroleum spirit, and solvent naphtha (coal-tar), and ordinary fractional distillation will not separate these.

The arrangement shown in Fig. 64 used by Engler in the fractional distillation of mineral oils lends itself to the fractional distillation of varnishes and destructive distillation of resins. Needless to say, the boiling-point of a spirit varnish is modified when it contains kauri or Manila copal from which the essential oil, of which they contain an appreciable extent, is not removed by previous fusion of the resin.

Determination of Boiling-point of Varnish.—This may be done by heating a certain quantity of varnish in a small flask, and collecting the vapours either in a condenser or in a flask containing water. A thermometer placed in the vapour indicates the boiling-point and consequently the nature of the solvent used. In cases where the analyst has only a very small quantity of varnish at his disposal, sometimes no more than an ounce, and where he may have to make numerous tests for comparative trial against the sample submitted, every drop of that sample is precious. Now in some cases, if the varnish were heated to the boiling-point of the solvent used, even when the heating vessel is attached to a reflux condenser, say in the case of a metallic rosinate, such as the magnificent green copper rosinate varnish, the green would be liable to become

reduced to a yellow passing to ruby-red. But if this be a point put to practical use by the porcelain and glass decorators, it is to the analyst, in determining boiling-points or in fractionally distilling such a varnish, only a source of annoyance, except in so far as the reduction of the copper indicates the source of the colouring principle. If the whole of the sample were thus used up and spoilt, the analyst would be left in the lurch. But the boiling-point may be determined sufficiently accurate for technical purposes without distillation, and by the use of only a single drop of liquid. The liquid is

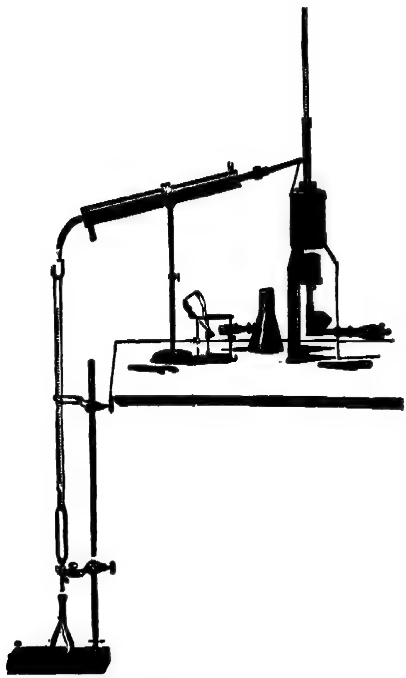


FIG. 64.—Fractionating Still, Condenser, and Graduated Receivers.

placed in a glass tube, drawn out and sealed at the bottom. A capillary tube, sealed up a little above its lower open extremity, is introduced, and the whole is attached to a thermometer, and treated as in the determination of a melting-point. Before the liquid reaches the boiling-point, single air-bubbles proceed from the small volume of air in the capillary below the closed constriction ; these become gradually more numerous till an uninterrupted thread of small bells of vapour is established. At this moment the thermometer shows the exact boiling-point of the liquid. The operation should be repeated several times and the mean of the observations taken. The capillary prevents boiling and must be renewed for each experiment.

CHAPTER XXVII.

THE DETERMINATION OF THE RESINS AND SOLVENTS IN SPIRIT VARNISHES.

Resin Determination.—The nature of the resin or resins forming the foundation or basis of spirit varnish, and on which the nature of the film or coat left on evaporation of the solvent depends, is determined in the residue either after evaporation or after distillation of the solvent. Its appearance and properties will afford valuable clues, provided always, on the one hand, that all the solvent has been got rid of by evaporation or distillation, and on the other hand that the distillation process has not been carried too far, so as to start the destructive distillation of the resin or resins, and finally that no chemical change has been produced causing either oxidation or reduction, polymerization or condensation (chemical). Otherwise, the characteristics of the original resins may be so altered in regard to colour, hardness, etc., as to prevent recognition. Anyone who has tried to evaporate a shellac spirit varnish, in a boiling water-bath, or even at a greater heat, knows how the last traces of the alcohol stick to the shellac like a leech, and also the alteration in properties which the shellac undergoes. Recovered shellac, that is, pure shellac recovered from its solution in alcohol, is no more genuine shellac than recovered rubber (that is, pure rubber recovered from its solution in a solvent) is genuine rubber. Both are much altered in properties. As to the alteration in shellac, James H. Stebbins, junior, a New York analyst, in order to recover the alcohol and shellac from a shellac spirit varnish, took a fractionating flask and measured out a given quantity of the varnish into the flask, which was then connected with a Liebig's condenser and immersed in a paraffin-bath which was heated at first to 100° C., the temperature being gradually increased to 130° C. The alcohol was gradually driven off into a receptacle and collected. The recovered alcohol smelled very strongly of shellac. Stebbins found samples of orange shellac and white shellac recovered in a molten state as the residue left in the still from above operation to be in both cases very hard and brittle, and in his opinion during the process of distillation the shellac seems to undergo some kind of a change whereby its solubility in alcohol is decreased, and for that reason he does not think it would be profitable for smugglers to recover either shellac or alcohol from spirit shellac varnishes. The writer's experience confirms

Stebbins' results. It must be remembered that alcohol is a basic body which, in combination with organic acids, forms ethereal salts, and the heat required for distillation is just that required for the alcohol to combine with the organic acids present in resins to form ethereal salts. Distillation or evaporation *in vacuo* therefore seems preferable to ordinary fractional distillation. Evaporation in the open air brings the factor of oxidation into play. But however recovered, no hard and fast conclusions can be drawn as to the nature of the resins used except in simple cases, and here physical tests such as the thumb-nail will often supplement a chemical analysis. The latter is not without giving valuable indications, more especially in the case of a spontaneously evaporated varnish. The solubility of such a film in ether, alcohol, carbon-disulphide, acetone, methyl alcohol, amylic alcohol, petroleum ether, benzene, chloroform, and spirits of turpentine, will give useful indications and serve as a source of comparison with the fractional distillation of the solvent from the varnish. Glacial acetic acid is used to identify mastic, that resin being the only one insoluble in that reagent. The solubility of the different resins in the solvents indicated is given on pp. 444, 445.

TABLE CLXXII.—OF THE SOLUBILITY OF RESINS IN ESSENTIAL OILS.[1]

100 parts by weight of undernoted Essential Oils dissolve	The following Resins in the undernoted proportions:—						
	Amber.	Rosin.	Copal.	Dammar.	Mastic.	Shellac.	Yellow Wax.
Cajeput . . .	6·53	43·70	5·52	42·49	41·16	0·66	—
Copaiba . .	—	24·95	8·0	34·57	—	—	4·49
Light camphor oil .	9·73	46·16	9·16	84·95	35·04	1·33	—
Heavy " .	6·50	31·35	2·81	50·08	37·98	0·83	—
Lavender . .	—	52·86	—	33·07	—	—	9·84
Cloves . . .	—	79·79	0·00	18·27	—	—	—
Rosemary . .	10·16	48·94	4·81	99·44	21·39	0·79	—
Allspice . . .	8·90	40·98	9·51	41·66	83·47	3·67	—
Turpentine . .	7·47	51·84	—	64·28	52·79	12·94	—
" rectified	10·30	—	6·47	—	—	—	8·10
Paraffin oil . .	—	—	—	9·27	—	—	4·16
Wax oil . .	2·87	—	—	67·31	—	—	5·64

The solubilities of the different resins entering into the composition of varnish may be so identical or so badly defined that no sound inference can be drawn by which they can be differentiated the one from the other. In such cases what is known as the *constants* of the resin have to be determined.

[1] The results here given must not be taken as absolute. They can only be true under the actual conditions of the experiment. Spirits of turpentine by continual agitation can be made to dissolve its own weight of rosin and is not then saturated even in the cold.

TABLE CLXXIII.—COMPARATIVE ACTION OF SOLVENTS UPON THE PRINCIPAL RESINS.

Resins.	Ether.	Alcohol.	Benzol.	Acetone.	Methylic Alcohol.	Amylic Alcohol.	Petroleum Ether.	Bisulphide of Carbon.	Chloroform.	Spirits of Turpentine.
Amber	Consists of 88 to 90 per cent of a resin completely insoluble in all solvents, and 12 per cent of a resin which dissolves more or less completely in alcohol ether, benzol, etc.									
Copals:—										
Hard: Zanzibar .	insoluble	insoluble	partially dissolve	insoluble	insol.	part. sol.	insol. or almost insol.	insoluble	part. sol.	The greater number are insoluble, but all are at least partially soluble in the oxidized essence; complete solution is effected by repeated treatment with oxidized spirits
Mozambique .	,,	,,		,,	,,			,,		
Madagascar .	,,	,,		,,	,,			,,		
Med. Hard: Sierra Leone .	,,	sol. 40 per cent		,,	,,			part. sol.		
Angola red .	partially soluble or yielding a jelly which dissolves on the addition of hot alcohol	partly sol.			,,					
Benguela .		almost completely soluble		partially soluble						
Angola bastard										
Pebble copal .					part. sol.					
Akkra . .										
Benin . .										
Loango . .										
Gaboon . .										
Congo . .										
Angola white .										
Soft, South American .	soluble	almost insol.								
Dammar	partly sol.	only part. sol. in the cold, sol. with the aid of heat	soluble	insoluble	partially soluble	partially sol.	soluble	partly sol.	soluble	soluble
Shellac	insoluble	soluble	almost insol.	,,	,,	,,	part. sol.	,,	insol.	part. sol.
Mastic	soluble	soluble in absolute, partly sol. in dilute, alcohol	soluble	partly sol.	,,	soluble	almost insol.	incomp. sol.	soluble	soluble in the hot
Sandarach	soluble	sol. in hot	almost insol.	almost insol. in cold, sol. in hot	,,	part. sol.	part. sol.	,,	part. sol.	incomp. sol.
Rosin	partly sol.	soluble	soluble	soluble	soluble	soluble	soluble	soluble	soluble	soluble
Elemi	,,	sol. in hot	,,	,,	,,	,,	,,	,,	,,	,,
Venice turpentine . .	,,	soluble	,,	,,	,,	,,	,,	,,	,,	part. sol.
Benzoin	,,	,,	insoluble	insoluble	part. sol.	part. sol.	part. sol.	insoluble	part. sol.	,,
Asphaltum	,,	only very par.	soluble	,,	insol.	,,	insoluble	,,	,,	,,

TABLE CLXXIV.—PERCENTAGE OF MATTER IN DIFFERENT RESINS INSOLUBLE IN THE USUAL VARNISH SOLVENTS (COFFIGNIER).

Resins.	Solvents.											
	Spirits of Turpentine.	Methylic Alcohol.	Ethylic Alcohol.	Amylic Alcohol.	Ordinary Ether.	Chloroform.	Acetone.	Benzene.	Carbon Tetrachloride.	Aniline.	Benzoic Aldehyde.	Amyl Acetate.
Copals :—												
Brazilian	48·20	30·20	38·20	1·80	29·70	36	37·60	40·50	44·90	8·30	26·70	3·40
Zanzibar	100	84·20	85·90	63·30	75	86·50	77·30	88·30	100·70	34·50	72·70	45·50
Madagascar	60·30	79·60	73·80	22·40	65	69	64·30	78·40	85	17·80	21·80	24·60
Demerara	92·50	77·40	72·10	53	55·40	56·90	69·20	70·90	75·50	73·90	50·20	37·10
Columbian	68·70	60	17·00	4·90	50	54·70	43·60	60·80	69·60	2·20	18·30	6
Benguela	68·80	46·90	16·50	0·90	43·70	47·30	24·80	65·60	61·30	0·90	14·10	1·20
Angola red	77	68	71·20	66·50	88·20	65·70	77·70	70	77·70	2·30	soluble	4·20
,, white	69·40	46·70	77	43·50	27·30	43·70	61	50·50	61·30	3·50	4·30	2·70
Congo	68·20	55·30	25·30	2·20	48·20	59·60	45·80	60·10	66·10	soluble	48·70	0·90
Pontianak	66·40	13·50	soluble	soluble	46	50·3	soluble	63	61·90	,,	soluble	soluble
Loango	—	—	—	—	—	—	—	—	—	—	—	—
Kissel	79·60	65·50	57·40	8·50	42·0	56·60	49·50	61·60	69·90	5·70	11·60	10·00
Akkra	79·70	62·80	47·80	4·10	44·0	66·00	45·80	66·90	80·30	2·50	10·10	7·40
Cameroon	78·60	78	66·70	19·20	55·50	66·60	60·50	71·80	73·70	8·40	22·80	12·00
Sierra Leone	71·40	49·20	62·30	4·80	47·80	52·40	40·30	56·90	70·90	0·70	1·50	soluble
Guapinol resin	77·30	—	58·00	60·60	55·90	—	57·10	—	—	21·40	—	—
Courbaril (Cayenne)	63·50	—	24·40	10·00	43·00	—	33·90	—	—	6·40	—	—
Manila, hard	73·20	64·60	55·90	soluble	58·50	36·70	52	63·90	69	soluble	1·10	soluble
,, friable, soft	64·10	7·30	soluble	,,	28·70	52·40	soluble	57·90	62	,,	1·70	,,
Kauri, pale	77·50	46·90	6·60	,,	61·80	54·40	8·90	66·70	81·10	,,	soluble	,,
,, brown	73·60	61·90	35·80	,,	60·70	58·78	38·70	70·60	77·30	,,	,,	2
,, bush	72·90	47·30	12·30	,,	55·10	50·70	20·70	61·70	71·90	,,	,,	soluble
Elemi	soluble	soluble	soluble	,,	soluble	soluble	leg. insol.	soluble	—	—	—	—
Java copal	—	—	—	—	—	,,	—	,,	—	—	—	—
Rosin	soluble	—	soluble	—	soluble	,,	soluble	,,	—	—	—	—
Galipot	—	—	,,	—	—	—	—	—	—	—	—	—
Burgundy pitch	soluble	—	,,	—	soluble	—	soluble	soluble	—	—	—	—
Stockholm tar	—	—	,,	soluble	,,	soluble	,,	—	—	—	—	—
Trinidad pitch	—	—	—	—	—	—	—	—	—	—	—	—
Dammar (Batavian)	soluble	—	28·60	12·40	3·80	soluble	soluble	soluble	soluble	—	—	—
Mastic	,,	—	36·20	soluble	soluble	,,	9·50	,,	,,	—	—	2·80
Sandarach	73·60	—	soluble	,,	,,	56·00	soluble	67·40	79·00	—	—	—
Madagascar copal, fused	3·60	93·30	91·80	66·70	51·80	1·70	84·80	1·50	4·00	indetermin.	2·00	51·20
,, solubilized by naphthalene	52·10	86·80	74·40	12·80	19·70	soluble	65·00	40·00	25·80	soluble	soluble	soluble
Turpentine (Venice)	soluble	—	soluble	—	soluble	—	—	—	—	—	—	—
,, (common)	,,	—	,,	—	,,	—	—	—	—	—	—	—

These are :—

1. *The Acid Value* (free acid), that is to say, the number of milligrammes of caustic potash required to exactly neutralize 1 gramme of resin in alcoholic solution. The acid figure is determined by heating 1 gramme of the finely pulverized resin with 95 per cent alcohol in a glass flask attached to a reflux condenser until complete solution is effected. Two c.c. of a dilute solution of phenol-phthalein are added, and the solution titrated with standard alkali.

Marcusson and Winterfield recommend the use of a mixture of equal parts of absolute alcohol and benzine as a solvent for resins in the determination of the acid value. This reagent dissolves out the free acids in a very short time and is preferable to repeated extraction with boiling alcohol. Some resins, e.g. kauri, Manila copal, mastic, sandarach, and elemi are completely dissolved by it. In the presence of rosinate of lime, 5 to 10 grains of the substance are heated under a reflux condenser with 50 c.c. of a mixture of 90 parts of benzol and 10 parts of absolute alcohol. The insoluble matter is filtered off, washed with 30 c.c. of alcohol, and the filtrate titrated with $\frac{N}{10}$ caustic potash, using phenol-phthalein till the lower layer becomes pink. In the presence of aluminium, iron, or manganese rosinates or linoleates 10 to 20 grammes of the sample are extracted with benzene, the solution filtered, and mixed with 30 c.c. of water to which a few drops of methyl orange have been added. The solution is titrated with $\frac{N}{2}$ hydrochloric acid till the aqueous solution remains pink after heating and shaking. This gives the amount of acid required to decompose the soaps of the metal. The aqueous layer is now drawn off and the benzene washed once with water, the benzene solution is then mixed with neutral alcohol and titrated with $\frac{N}{10}$ caustic soda, using phenol-phthalein. This gives the amount of alkali required to neutralize both the combined and the free resin acids. If from this be deducted an amount of alkali equal to the hydrochloric acid used, the remainder will be due to the free resin acids.

2. *The Köttstorfer Value* (corresponding to the total acids after complete saponification, that is to say, the number of milligrammes of caustic potash required to saturate 1 gramme of resin in alcoholic solution in presence of an excess of potash). The Köttstorfer value is determined by heating 1 gramme of the resin with 25 c.c. of standard alcoholic potash from five to fifteen minutes in a flask attached to a reflux condenser; the whole is then diluted with 100 c.c. of alcohol and again brought to the boil, and the uncombined alkali is titrated back with standard hydrochloric acid in presence of phenol-phthalein.

3. *The Ester Value* is got by deducting the acid value from the Köttstorfer.

4. *The Hübl or Iodine Value,* i.e. the weight of iodine fixed or absorbed by 100 parts of resin in alcoholic solution.

Process.—One gramme of resin is dissolved in 50 c.c. of hot alcohol and cooled, and 50 c.c. of a standard solution of iodine, 25 grammes I, 30 grammes $HgCl_2$, 500 c.c. alcohol added. If the iodine be decolorized, a fresh quantity of the iodine solution is added until the mixture becomes of a permanent red-brown colour. The whole is allowed to stand for twenty-four hours, after which the iodine in excess is estimated in the following manner: A solution of potassium iodide is added until on the addition of water or a salt of mercury no further precipitate of iodine or mercuric iodide is obtained. Too great an excess must be avoided. The liquid is then diluted with 5 to 6 volumes of water. The resin separates in flocks. Starch paste is added and the solution titrated with hyposulphite of soda. The end of the operation is indicated by the decoloration of the iodide of starch.

When the resin is not completely soluble in alcohol the solution is thrown upon a tared filter, washed with boiling alcohol, and the residue dried at 100°. With resins insoluble or difficultly soluble in alcohol, spirits of turpentine is used as the solvent. The solution is filtered and the insoluble residue weighed; the solvent is distilled in a current of steam, and the residue treated as in the preceding paragraph.

In this case the acid figure and the Köttstorfer figure are always a little low, for a portion of the free acids is carried away in the distillation process. The quantity of iodine absorbed is on the contrary a little too high.

Von Schmidt and Erban, in order to show that their results were of practical value in the quantitative estimation of resin, made the following researches: (1) A mixture was made consisting of 40·64 per cent of sandarach and 59·36 per cent of mastic. As these resins are very different in acid number, they are very suitable for gravimetric analysis. Two tests of the mixture gave the numbers 95·167 to 95·8, showing a mean of 95·483. If the percentage of sandarach present is denoted by X, we get the equation $141{\cdot}05\,X + 64{\cdot}05\,(100 - X) = 95{\cdot}483{\cdot}100$. This gives for X 41·36 instead of 40·64, and therefore 58·64 for the mastic instead of 59·36 per cent. (2) A mixture was tested made of 57·25 per cent of dammar (X) and 42·75 per cent of used red Angola copal. In this case the greatest difference is in the saponification numbers, and the greatest value was therefore attached to them. Two estimations gave the numbers 72·259 and 73·619 respectively, a mean of 72·934. From the equation $46{\cdot}8\,X + 110{\cdot}25\,(:100 - X) = 72{\cdot}934{\cdot}100$ we get 58·81 instead of 57·25 for the dammar and 42·75 for the copal. (3) A mixture was made of 68·59 per cent of shellac and 31·41 of rosin (X). This is a very easy example, remembering that shellac has no iodine number. The mean determination of the iodine number of the mixture was 35·43, which gives 30·62 per cent of rosin instead of 31·41 per cent. (4) To see how far the accuracy of the methods

was affected by precipitating the mixed resins from solution, a varnish was made by dissolving 38·01 parts of rosin, 28·65 parts of dammar, and 33·34 parts of mastic in oil of turpentine. The solvent was removed by hydrogen, and the precipitated resins were dried on the water-bath and their relative proportions determined. The numbers obtained were: Rosin 38·8, dammar 30·74, and mastic 30·96, the greatest error being thus 2·4 per cent. As the errors of experiment are multiplied in the necessary subsequent arithmetical calculation, and as the number of these operations necessary increases with the number of resins in the mixture, the results cannot be relied upon for more than three resins at the most.

TABLE CLXXV.—SCHMIDT AND ERBAN'S TABLE OF CONSTANTS.

Resin.	Acid Value.	Saponification Value.	Iodine Value. With Residue.	Iodine Value. Without.
Rosin, indigenous	146·5 145·5	168·2 166	— —	116·8 114·8
Sandarach	141·4 138·7	174·4 170	— —	66·8 63·8
Benzoin	136·3 134·1	164·7 164·5	— —	57·4 56·6
Storax	130·6 128·5	205·6 191·0	64·7	58·6
Fused Angola, white	93·6 93·4	118·8 117·8	44·9	41·6
Gamboge	81·2 79·4	non-determinable	70·9	70
Venice turpentine	70·1 69·3	102·6 96·4	— —	145·3 141·9
Shellac, brown	65·1	213·8	8·3	6
„ orange	60	211·6	—	0
Mastic	64·5 63·6	93·8 92·3	64·4 64·2	58·2 53·1
Dammar	33 30·6	47·1 46·5	63·6 63·5	64·1 60·5
Fused red Angola	30·5 30	110·7 109·8	34·8	22·3
Elemi	22·3 22	25·1 24·0	— —	85·1 80·9
Dragon's blood	non-determinable	—	72·4	55·5
Red Angola	—	148 146·4	— —	— —
Amber	—	145 144·6	— —	— —
White Angola	—	132·2 129·7	— —	— —
Zanzibar copal	—	92·4 9·6	— —	— —
Fused amber	0	38·2 33·9	4·8	3·3
Fused Zanzibar	0	36·8 34·6	12·6	7·6
Asphaltum	0	8·1 1·3	22·2	3·5

TABLE CLXXVI.—SHOWING THE ACID, SAPONIFICATION, AND ESTER NUMBERS OF CERTAIN RESINS (KREMEL).

Resin.	Acid Number.	Saponification Number.	Ester Number.
Rosin (German)	151·1	—	—
Sandarach	144·2	—	—
Benjamin (Siam)	141·1	196·5	55·4
Gamboge	100·0	156·7	56·7
Shellac	65·5	115·7	50·2
Mastic	{ 61·08 70·09	—	—
Dammar	{ 31·0 34·3	—	—
Elemi	17·6	25·4	7·8
African copal	147·8	—	—
Amber	{ 33·4 34·4	108·9 124·5	74·5 91·1
Copal (sort unknown)	132·0	—	—
Zanzibar copal	{ 85·3 80·9	—	—

Kremel wrought independently of Schmidt and Erban, and his results are in very fair accordance. Where he differs from them mostly is because he dissolved those resins which are difficultly soluble in alcohol in ether or chloroform, whereas the other chemists used merely solutions in alcohol. Kremel's results are given above.

TABLE CLXXVII.—MOISTURE SOLUBILITY AND CHEMICAL CONSTANTS OF SPIRIT VARNISH RESINS.

	Water.	Insoluble in Alcohol.	Acid Value.		Saponification Value.	
			Crude Resin.	Purified Resin.	Crude Resin.	Purified Resin.
Shellac	3·79	14·40	39·2	56	212·8	226·8
Seed lac	2·63	10·69	58	56	218·4	224
Yellow accroides	5·65	0·03	82·3	64	98	106
Red "	4·90	5·26	18·5	25	64·4	106
Sandarach	2	0·54	137·2	137·8	162·4	170·8
Soft Manila	2·10	2·30	136·6	150	187·6	187·6
Hard "	1·68	3·39	138·9	—	215·6	—
French rosin	0·80	0·10	169·7	—	177·8	—
American "	0·75	0·20	73·9	—	121·8	—
Elemi	0·20	0·10	22·4	—	28	—

TABLE CLXXVIII.—SHOWING CHEMICAL AND PHYSICAL PROPERTIES OF VARNISH RESINS.

	Density.	Softening of the Non-dried Substance. °C.	Fusion of the Dry Substance. °C.	Saponification Value. Hot.	Saponification Value. Cold.	Acid Value.	Köttstorfer Value.	Iodine Value.
Amber	1·080	—	280-315	86·8 W-145 S	—	15·4 W	144·6-145	62·10 W
,, fused	—	—	—	38·2 S	—	—	—	4·83
Copal, Zanzibar	1·058 C	—	259 Bo-360 Bo	92·4 S	—	86·8 C-93	70·1-76·1	—
,, ,, fused	—	—	—	36·8 S	—	61·6 C	67·7 C-72·9 C	126·8
Madagascar	1·056 C	—	7300 C	—	—	—	—	—
,, fused	1·062 C	—	—	—	—	68·2 C	44·9 C	—
,, solubilized by naphthalene	1·061 C	—	—	—	—	68 C	65·9 C	—
Demerara	1·047 C	90 C	180·0 C	—	—	97·7 C	102·4 C	—
Java copal	1·033 D-1·041 D	—	175-180 D	14·54 D-18·03 D	—	4·55 D-5·07 D	—	50·36 D-54·66 D
Benguela	1·058 C	65 C-95	140-165 C	140-168	145·6-162·4	134·1-137·2	—	60·59-85·1 S
,, A	1·066 C	—	180-185 C	—	—	123·1 C	157·1 C	—
,, B	1·041-1·062	—	215	—	—	129·8 C-130·5 C	134·6 C	—
,, fused	—	—	—	—	—	103·3 C-110·5 C	101 C	—
Sierra Leone	—	100-110	130-135	138·5 W-156·8	145·6-168	72·8 W-120·4	—	63·49-133·35 W
,, A	1·0645 C	—	195 C	—	—	84·6 C	—	—
,, B	1·066 C-1·075 C	—	200 C	—	—	129·3-130 C	129·3-131·8 C	—
,, fused	—	—	—	—	—	—	—	—
Red Angola	1·066 C-1·068 C	90 C-120	145-315 C	131·8 C-162·4	115·8-168	128·8-142·7 C	146·4 C-148 C	63·29-136·9 W
,, fused	—	—	—	119·7 S	—	30·5 S	—	34·8 S
Angola, white	1·055 C	—	95 C-125 Ba	132·2 S	—	57·4 W-127 C	133-159 C	129·66 W
,, fused	—	—	—	118·8 S	—	93·6 S	—	44·9 S
Congo	—	90 C-95	115-195 C	162·4-179·2	184·8-196	132·3 C-151·2	131·8 C	58·41-59·12
Akkra	1·033 C	105	120 C-155	140·4-168	145·6-168	97·8 C-128·8	140 C	61-62·19
,, red	—	—	—	—	—	46·2	131·6	—
Kissel	1·066 C	—	110 C	—	—	70·4 C	117·8 C	—
Benin	—	115	155	140-156·8	140-145·6	112-128·8	—	58·34-58·86
Cameroon	—	96 Bo-110 Bo	110 Bo-150 C	151·2-162·4	162·4-168·4	128·8-159·7 C	70 C	65·25-69·96
Loango	—	75	100	151·2-156·8	151·2-162·4	112-123·2	—	59·52-60·87
Brazil	1·053 C	50 C	100 C	—	—	123 C-129·5	133 C-143	—
Columbia	1·054 C	90	7300	—	—	118·8 C	155·7 C	—
Guapinol	1·033 C	—	—	—	—	117·8-119·6 C	129 C	—
Courbaril	1·059 C	—	—	—	—	129·8 C-130·1 C	157 C	—
Kauri, pale	1·036	75	165 C	—	—	70·9 C-78·3 C	89·6-98·1 C	—
,, fused	—	—	—	—	—	72·3 C-75·2 C	72·9 C	—
,, bush	1·030	—	—	—	—	79·2 C-81·2 C	78·5 C	—
,, fused	—	—	—	—	—	64·9 C-68·9 C	89·7 C-95·3 C	—

TABLE CLXXIX.—SHOWING CHEMICAL AND PHYSICAL PROPERTIES OF SPIRIT VARNISH RESINS.

	Density.	Points of: Softening of Non-dried Substance. °C.	Points of: Fusion of the Substance Dried. °C.	Saponification Value: Hot.	Saponification Value: Cold.	Acid Value.	Köttstorfer Value.	Iodine Value.
Kauri, 1st quality	—	—	—	—	—	92·8 C-93·8 C	87·7 C-92·5 C	—
,, ,, fused	—	—	—	—	—	86·7 C-87·7 C	86·7 C	—
,, brown	1·053	90	185 C	—	—	78·8 C	81·7 C	119·5 L
Turpentine, common	0·856	—	130	—	—	—	—	—
,, Venice	—	—	—	—	—	69·8	99·6	143·6
Manila, hard	1·065 C	80 C	190 C	227·1 D	—	72·80 C	87 C	90·6 D
,, soft	1·060 C	45 C	120 C	—	—	145·2 C	185·1 C	—
,, Borneo	—	—	145	—	—	141·4 C-144	176·7 C-179·5	138·04 W
,, ,, B-hard	1·074 C	—	135	176·7 W	—	161·3 C-163	168·3 C-173·9 C	—
,, ,, semi-hard	1·047 C	—	110	—	—	152·4 C-154·7	151·4 C	—
,, Singapore	—	—	—	194·1 W	—	128·8 W	194	123·31 W
Dammar, Assam	—	—	—	9·43	—	8·15	—	—
,, Batavia	1·031 C	—	100	31·1 W-47·1 S	—	21 W-35·5 C	39·2 C	63·6 S-142·24 W
Mastic	1·057 C	—	95 C	79·1 W-193·8 S	—	50·4 W-64·4 S	70·1 C-93·8	64·4-159 W
Pontianak	1·037 C	55 C	135 C	—	—	134·3 C	186·5 C	—
Sandarach	1·073 C	—	145 C	155·4 W-174·4 S	163·1-166·25	141·4 S-154 W	142·1-174·4	66·8 S-160·6 L
Accroides	—	—	—	—	—	—	—	119·3 L
Elemi	—	—	—	28·6 S	—	15·7 W-22·3	24-25·1	80·9-175·39 W
Benjoin	—	—	—	148·4 W-164·7 S	—	98 W-136·3 S	164·5	57·4 S-76·45 W
Storax	—	—	—	205·6 S	—	128·5-130·6 S	191-205·6	64·7 S
Shellac, average	—	—	—	203·3 W-213·3 S	—	63 W-65·1 S	—	8·3 S-24·62 W
,, fine	—	—	—	212·6 W	—	56 W-60	211·6	28·70 W
,, orange	—	—	—	206·4 W-211·6 S	—	60 S-64·4 W	—	15·8 L-17·7 L
,, pale	—	—	—	211·4 W	—	56 W	—	19·81 W
,, good quality	—	—	—	210·7 W	—	47·6 W	—	20·40 W
,, bad ,,	—	—	—	193·8 S-194·1 W	—	57·4 W	—	19·05 W
Asphaltum, natural	1·070-1·150	—	environ 100°	8·1 S	—	—	1·3-8·1	22·2 S
,, Manjak	1·123 C	—	233 C	—	—	—	—	—
,, Syrian	—	—	—	23·7 S	—	8·9 W	—	—
Trinidad pitch	1·123	—	215 C	—	—	—	—	—
Dragon's blood	—	—	—	153·4 S	—	11·2 W	153·4	54·08 W-72·4 S
Rosin, ordinary	1·07	80	100	168·2 S-190·1 W	—	146·5 S-169·4 W	167-187·4	112·01 W-172·6 S
,, refined	—	—	—	187·4 W-195·7 W	—	177·8 W-179·2 W	—	114·8 W-115·8 W
Gamboge	—	—	—	—	—	79·4-81·2	147·8	70·9

Ba = Bamberger; Bo = Bottler; C = Coffignier; D = Dieterich; L = Langmuir; S = Schmidt and Erban; W = Williams.

TABLE CLXXX.—CHEMICAL CONSTANTS OF RESINS.

	Acid Value.			Saponification Value.			Iodine Value.	
	Schmidt and Erban.	Williams.	Coffignier and others.	Schmidt and Erban.	Williams.	Coffignier and others.	Schmidt and Erban.	Williams.
Rosin, common	146·5	169·4	—	168·2	176·4	—	116·8	112·01
Common	—	166·6	—	—	190·1	—	Other Observers 126·7-172·6	113·28
Refined	—	179·2	—	—	187·4	—	Langmuir 175·7-	115·31
,,	—	177·8	—	—	195·7	—	262·5	114·80
Shellac, medium	65·1	63·0	—	213·3	203·3	—	8·3	24·62
Garnet	—	56·0	—	—	212·6	—	—	28·70
Orange	60·0	64·4	—	211·6	206·4	—	Langmuir 15·8-17·7	17·52
Good	—	47·6	—	—	210·7	—	—	20·40
Light	—	56·0	—	—	211·4	—	—	19·81
Bad	—	57·4	—	—	194·1	—	—	19·05
Sandarach	141·4	154·0	—	174·4	155·4	—	66·8	—
,,	—	145·6	—	—	157·0	—	Langmuir 160·6-174·8	134·30
Mastic	64·4	50·4	—	193·8	73·4	—	64·4	158·62
,,	—	56·0	—	—	79·1	—	—	159·00
Dammar, Batavia	—	22·4	—	—	36·4	—	—	117·67
,,	33·0	26·6	33-72	47·1	31·1	33-72	63·6	142·24
,,	—	21·0	—	—	40·7	—	—	130·24
Benzoin	136·3	98·0	—	164·7	148·4	—	57·4	76·45
Storax	130·6	—	—	205·6	—	—	64·7	—
Venice turpentine	—	—	—	—	—	—	—	—
Copal, Angola, white	—	57·4	127	132·2	133·0	159·9	—	129·66
,, ,, melted	93·6	—	—	118·8	—	—	44·9	—
,, ,, red	—	60·2	128·3	148·0	136·2	131·8	—	136·90
,, ,, melted	30·5	—	—	119·7	—	—	34·8	—
Zanzibar	—	—	—	92·4	—	—	—	—
,, melted	—	—	—	36·8	—	—	12·6	—
Borneo	—	141·4	—	—	176·7	—	—	138·04
Singapore	—	128·8	—	—	194·1	—	—	123·31
Sierra Leone	—	72·8	110·2	—	138·5	123·4	—	133·35
,, purified	—	84·0	—	—	129·0	—	—	138·04
Akkra	—	46·2	—	—	131·6	—	—	121·66
Benguela	22·3	—	123·1	25·1	—	157·1	85·1	—
Congo	—	—	132·3	—	—	131·8	—	—
Unknown	—	57·4	—	122·2	—	—	—	142·24
Elemi	—	15·7	—	28·6	—	—	—	175·39
Amber	—	15·4	—	145·0	86·8	—	—	62·10
Melted	—	—	—	38·2	—	—	4·8	—
Anime, Zanzibar	—	18·2	—	—	73·6	—	—	135·25
Copal, Manila	—	131·6	—	—	181·4	—	—	137·79
Asphaltum	—	—	—	8·1	—	—	22·2	—
Syrian	—	8·9	—	23·7	—	—	—	—
Dragon's blood	—	11·2	—	153·4	—	—	72·4	54·08
India-rubber	81·2	—	—	—	—	—	70·9	98·42
Gum-arabic	—	8·4	—	—	84·0	—	—	—
,,	—	2·8	—	—	56·7	—	—	0·51
,,	—	2·2	—	—	89·7	—	—	—
Gum Senegal	—	2·8	—	—	104·2	—	—	5·59
Tragacanth	—	1·4	—	—	110·5	—	—	—
,,	—	1·4	—	—	119·8	—	—	1·16
Kauri	—	—	—	—	—	—	Langmuir 119·5	—
Accroides	—	—	—	—	—	—	119·3	—

The iodine values by Langmuir were estimated by the method of Wijs.

Qualitative Analyses of Resins—Hirschsohn's Scheme.—The following tables (pp. 454 *et seq.*) are summarized from the elaborate scheme of Hirschsohn's reagents :—

(1) Sulphuric acid H_2SO_4, specific gravity 1·820. (2) Alcoholic hydrochloric acid (95 per cent alcohol saturated with *dry* HCl). (3) Bromine, 1 in 20 of chloroform. (4) Saturated solution of bleaching powder in distilled water at ordinary temperature. (5) One part of ferric chloride Fe_2Cl_6 in 10 of 95 per cent alcohol. (6) Saturated solution of *neutral* lead acetate $Pb(A_2)$ in 95 per cent alcohol. (7) Solution of ammonia, specific gravity ·980. (8) Solution of pure Na_2CO_3 in distilled water. (9) Frohde's test, 1 centigramme sodium molybdate in 1 c.c. sulphuric acid. (10) Impure chloral hydrate containing alcoholate. (11) Saturated solution of iodine in petroleum spirit boiling at 60° C. (12) Petroleum spirit boiling between 35° and 40° C.

TABLE CLXXXI.—QUALITATIVE ANALYSES OF RESINS (HIRSCHSOHN).

GROUP I.—COMPLETELY SOLUBLE IN CHLOROFORM.

Sub-Group I.—*Completely Soluble in Ether.*

Experiment.	Observation.	Inference.
Add alcohol to ethereal solution.	A.—Turbidity (if none pass on to B.).	
Add Fe_2Cl_6 to alcoholic solution.	I. Turbidity disappears on boiling.	
Treat with chloral.	Violet coloration.	Canada balsam.
	II. No turbidity.	
	(a) The resin is liquid.	
Treat with own vol. petrol. spirit.	Dissolves.	
Add bromine test to chloroform solution.	1. Yellowish, passing through violet to blue coloration.	Maranham copaiba.
	2. No colour.	Para copaiba.
	(b) The resin is solid.	
Treat with petrol. spirit.	Dissolves partially.	
Treat with iodine solution.	Red-violet coloration.	Mastic (ordinary).
Add alcohol to ethereal solution.	B.—Clear solution.	
Treat resin with alcohol.	I. Dissolves completely (if not pass on to II.).	
Add Fe_2Cl_6 to alcoholic solution.	1. Blue coloration.	
[Add $Pb(A)_2$ to alcoholic solution.	(a) Precipitate.—H_2SO_4 dissolves resin with a cherry-red coloration.	Guaiacum.
	(b) No precipitate.—H_2SO_4 solution yellowish-brown.	Caranna resin (Aceyta Americana.
,,	2. Brownish or greenish coloration.	
	(a) Precipitate (if none pass on to (c)) not dissolved on boiling (if it dissolves pass on to (b)).	
[Treat resin with solution of Na_2CO_3.	(1) Dissolves partially at ordinary temperature.	
Dissolve resin in petrol. spirit, evaporate solvent, test residue with chloral.	Gradually becomes reddish-violet with blue streaks.	Coniferous resins and balsams.
	(2) Little or no action.	
,,	i. Colourless. Chloral test faint green.	Bombay mastic.
,,	ii. Dark brown. Chloral test brown.	Mani resin.
,,	iii. Yellow-brown. Chloral test dull violet.	Caranna resin.
,,	iv. Yellow-brown. Chloral test and bromine solution a magnificent violet.	Caranna hedionda.
[Add $Pb(A)_2$ to alcoholic solution.]	(b) Precipitate dissolves on boiling.	

GROUP I.—COMPLETELY SOLUBLE IN CHLOROFORM (*Continued*).

SUB-GROUP I.—*Completely Soluble in Ether* (*Continued*).

Experiment.	Observation.	Inference.
[Bromine solution.]	(*a*) Red coloration.	Peruvian guaiacum.
	(*b*) No coloration.	Alexandria mastic.
[Add $Pb(A)_2$ to alcoholic solution.]	No precipitate. Ammonia gives turbidity.	Dragon's blood.
Treat resin with alcohol.	II. Imperfect solution.	
[Add $Pb(A)_2$ to alcoholic solution.]	(1) Turbidity which disappears on warming.	Brazilian copaiba.
	(2) No precipitate. Resin crystalline. Does not dissolve on boiling Na_2CO_3.	
[Bromine solution.]	(*a*) Gradually colours green.	
[Alcoholic HCl.]	Colours violet, blue, or brown.	Elemi.
	(*b*) Colours violet.	Elemi.
	(*c*) No colour.	Elemi (Amyris Elemifera).

GROUP I., SUB-GROUP II.—*Imperfectly Soluble in Ether.*

Experiment	Observation	Inference
Treat resin with alcohol.	A.—Dissolves perfectly.	
Treat evaporation residue of a petrol. spirit extract with H_2SO_4.	I. Cherry-red coloration. No cinnamic acid.	Siam benzoin.
	II. No coloration or faint brown, contains cinnamic acid.	Sumatra benzoin. Tolu balsam.
	III. Yellow-brown passing to violet.	Black Peru balsam.
	B.—Incomplete solution.	
Add Fe_2Cl_6 to alcoholic solution.	I. Precipitate does not re-dissolve on boiling and is insoluble in ether.	Brazilian copal.
	II. No turbidity or slight disappearing on boiling.	
Add alcohol to ethereal solution of resin.	1. Turbidity.	
Alcoholic HCl	(*a*) Brownish coloration.	
Treat with chloral evaporation residue of petrol. spirit extract.	(1) Greenish coloration.	Dammar.
	(*b*) Brick-red.	
"	(2) Carmine-red to violet.	White Peru balsam.
	2. Clear solution.	
	(*a*) Clear solution.	
Add ammonia to alcoholic solution.	(1) Blue coloration.	Ceradia resin.
Add bromine to alcoholic solution.	(*b*) Turbid solution.	
"	(2) Greenish coloration.	Mecca balsam.

GROUP II.—IMPERFECTLY SOLUBLE OR INSOLUBLE IN CHLOROFORM.

SUB-GROUP I.—*Completely Soluble in Ether.*

Experiment	Observation	Inference.
Treat resin with ether.	1. A clear solution. Red solution. No turbidity.	Dragon's boold, from Pterocarpus Draco.
Add ammonia to alcoholic solution.	2. Solution yellow or colourless.	
To alcoholic solution add $Pb(A)_2$.	(*a*) No precipitate.	Podocarpus resin.
	(*b*) A precipitate permanent on boiling.	Sandarach.

SUB-GROUP II.—*Imperfectly Soluble in Ether.*

Experiment	Observation	Inference
Treat ether solution with alcohol.	A.—Turbidity	
Add ammonia to alcoholic solution.	I. A clear mixture.	
	1. The mixture is yellow.	
Dissolve resin H_2SO_4.	Solution yellowish-brown, and gives clear violet mixture with alcohol.	Eryops resin.
	2 The mixture is carmine-red.	Sonora lac.
	II. A turbid mixture.	
Fe_2Cl_6	1. Green colour. The drug contains cinnamic acid.	
$Pb(A)_2$.	A precipitate.	Liquid storax.
	2. Brownish or not at all.	
	(*a*) The drug contains cinnamic acid.	
$Pb(A)_2$.	(1) No precipitate.	Liquidambar balsam.
	(*b*) The drug does not contain cinnamic acid.	
$Pb(A)_2$.	(2) No precipitate.	Euphorbia Tirucalli resin.
Treat ether solution of resin with alcohol	B.—No turbidity.	
Treat resin with alcohol.	I Complete solution.	
Fe_2Cl_6.	Dark brown or black.	
	1. Alcohol solution red.	
$Pb(A)_2$	(*a*) No precipitate.	Xanthorrhœa Quadrangularis resin.
Chloroform extract.	(1) Colourless	
$Pb(A)_2$.	(*b*) Turbidity.	
Chloroform extract.	(2) Yellow	Xanthorrhœa Arborea.
	2 Alcohol solution yellow	
$Pb(A)_2$.	A precipitate.	Yellow xanthorrhœa.

Sub-Group II.—*Imperfectly Soluble in Ether* (*Continued*).

Experiment	Observation.	Inference.
	II. Incomplete solution.	
Treat alcohol solution of resin with ammonia.	1. Clear mixture. (1) Violet.	
$Pb(A)_2$.	Violet precipitate.	Shellac.
	(2) Yellow or colourless solution.	
Add Fe_2Cl_6 to alcoholic extract.	I. Black coloration.	
$Pb(A)_2$.	No precipitate.	Gamboge.
,,	2. Precipitate which neither dissolves on heating nor soluble in ether.	
$Pb(A)_2$	No precipitate.	
Treat resin with mixture of alcohol and ether.	(a) Dissolves easily.	
Treat chloroform solution of resin with bromine solution.	i. Precipitates resin completely.	Australian copal (? Kauri).
	ii. No precipitate.	Manila copal.
	(b) Dissolves imperfectly.	African copal.
Treat alcoholic solution of resin with ammonia	Turbidity.	
Fe_2Cl_6.	(a) Precipitate insoluble on boiling and in hot ether.	Borneo copal.
	(b) No precipitate.	
Treat resin with mixture of alcohol and ether.	(1) Dissolves completely.	
Treat petrol. spirit extract with chloral.	Blue to blue-violet coloration.	Balsam of *Liquidambar* Straciflua.
	(2) Dissolves incompletely.	
	I. The resin contains sulphur.	
Subject resin to dry distillation.	i. Yields umbelliferone.	
Treat petrol. spirit extract with HCl.	(a) Orange coloration.	
,, chloral hydrate.	Green coloration.	Persian Sagapenum.
,, HCl.	(b) Blue-violet.	
,, Chloral hydrate	Rose colour to raspberry-red and violet	Levant Sagapenum.
,, HCl	(c) No coloration.	
Treat resin with H_2SO_4.	Dissolves with yellow-brown colour and blue fluorescence.	
Treat resin with HNO_3.	Malachite green.	Ordinary asafœtida.
	ii. Yields no umbelliferone.	
Treat resin with Na_2CO_3 solution	(a) Bright brown extract on which acetic produces no change.	Asafœtida from ferula alliacea.
$Pb(A)_2$.	No precipitate.	

Sub-Group II.—*Imperfectly Soluble in Ether* (*Continued*).

Experiment.	Observation.	Inference
	(*b*) Emulsion which cannot be filtered.	
$Pb(A)_2$.	(1) No precipitate. Iodine no action.	Indian bdellium.
	(2) Precipitate immediate or in short time. Re-dissolves on heating.	
	Iodine no change.	African bdellium.
	II. The resin contains no sulphur.	
Subject resin to dry distillation.	(1) Yields umbelliferone.	
Treat petrol. spirit extract with HCl.	Is coloured.	
	(*a*) Orange	
,, chloral.	Green.	Persian galbanum.
,, HCl.	(*b*) Violet-red.	Comparatively fresh commercial (Levant) galbanum.
,, chloral.	Green.	
,, HCl.	(*c*) Violet-blue.	
Treat petrol. spirit extract with chloral.	Carmine-red.	Levant galbanum, older.
,, HCl.	(*d*) No colour.	African ammoniacum.
,, chloral.	Light brown	
	(2) Yields no umbelliferone.	
Treat resin with solution of bleaching powder.	(*a*) Orange-yellow coloration	Persian ammoniacum.
	(*b*) No coloration.	
$Pb(A)_2$.	1 No precipitate.	
Iodine.	i Change.	
Chloral.	Greenish	Olibanum.
Iodine.	ii. Not altered.	
Chloral.	No coloration	Indian myrrh.
$Pb(A)_2$.	2. Precipitate	
Bromine.	(*a*) Violet-red coloration.	Ordinary myrrh.
Chloral.	Violet.	
Bromine.	(*b*) No coloration or only yellowish.	
Fe_2Cl_6.	(1) Green.	Opoponax.
,,	(2) Brownish.	Euphorbium.

E. Hirschsohn has given particulars of four analyses made by him of the resins in varnishes according to the principles embodied in his scheme. The four substances analysed were lettered A, B, C, and D. They were all of a more or less intense yellow colour, and all possessed a distinct odour of impure wood-spirit. Before analysis each varnish was diluted with four times its bulk of 95 per cent alcohol. Each one, when treated with excess of ammonia, gave a clear solution; but, while the colour in A, C, and D became a cherry-

red, that of B changed to blood-red. A solution of chloride of iron in alcohol, 10 per cent, altered the yellow colour of B to brown, and that of A, C, and D to a greenish-black, but in all cases the liquid remained perfectly clear. Alcoholic solution of acetate of lead gave in all four cases a reddish-violet precipitate, except in B, where the precipitate was flesh-coloured. On boiling up no solution of precipitate appeared except in B. Hirschsohn explains these appearances in the following manner: The absence of any precipitate with ammonia shows that the only substance whose presence is possible are coniferous resins, dragon's blood from pterocarpus, sonora lac, gum lac, gamboge, sandarach, xanthorrhœa resin and all kinds of copals. The absence of a precipitate with chloride of iron shows the absence of seed lac. The colouring of the varnishes by chloride of iron to greenish-black, and the red colours with ammonia, showed the presence of gum lac. The behaviour to acetate of lead is even more distinctive than the colouring, for only gum lac gives with that reagent a reddish-violet precipitate. To get further proofs Hirschsohn distilled larger quantities of the varnishes over a water-bath. The distillate smelt of methyl alcohol, and made a clear mixture with water, showing that it contained no turpentine or other ethereal oils. It consisted, in fact, of simple denaturated spirit. The residue was only entirely soluble in petroleum ether in the case of B. The ether solution evaporated, gave a residue which was turned yellowish-brown by concentrated sulphuric acid, and dissolved easily in alcohol, giving a solution precipitated by alcoholic lead acetate. Other portions of the residue were dissolved in a hot ammoniacal solution of sodium carbonate, and the resin was precipitated from the solution in flakes by adding acid. Chloral and the residue produced a bluish-violet colour, which gradually became a deep blue. All these reactions show the presence of conifer resin in B. The insolubility of A, C, and D in petroleum ether shows the absence of conifer resin, gamboge, guajac, sandarach and xanthorrhœa resin. If dragon's blood or sandalwood had been present, the extract would have been reddish, and fluorescent if sandalwood were present. The conclusions, then, are that the varnishes A, C, and D were simply solutions of gum lac in spirit, while B also contained colophony. Rosin can be separated from shellac by taking advantage of the fact that the former is almost entirely soluble in petroleum ether, while the latter is insoluble therein.

Gill's Scheme for the Analysis of Varnish.—A. H. Gill eliminates the turps by distillation with steam and the oil by Twitchell's process, thus obtaining pure resins which are examined first by Hubl's method, Table I., then by McIlhiney's bromide method, Table II., and finally, and most satisfactorily, the saponification, free acid, and ester values, Table V., are determined.

Elimination and Determination of the Turps.—Sixty grammes of the varnish are weighed into a 500 c.c. round-bottomed flask, this connected with a condenser and a two-quart can which furnishes steam;

the varnish is warmed just above 100° by a small flame and kept at this point to prevent condensation of steam used for distillation, which is continued until about 500 c.c. water have passed or until only a faint odour of turpentine in last portions of distillate. With a pure rosin varnish only a small portion of the resin sticks to flask, while with pure copal varnish the resin coats inside of flask almost completely. The solvent is separated from the water, dried by anhydrous sodium sulphate, distilled and weighed. The specific gravity gives a fair idea of its purity. The residue in flask is boiled for an hour over a free flame at a reflux condenser with 150 c.c. of normal alcoholic potash made from absolute alcohol and "potash purified by alcohol". Care is taken to warm flask very slowly or on water-bath first, to prevent bumping: the solution is cooled, separated from residue and the latter again treated with potash solution, repeating until complete saponification takes place. Usually a residue of about 1 per cent remains. The solutions are united in a separating funnel neutralized by hydrochloric acid, causing a precipitate of potassium and lead chlorides, the latter from the drier, water and ether are now added, the latter dissolving the fatty acids and resins liberated by the acid. The ethereal solution is run into a flask, the ether distilled off and a small quantity of absolute alcohol added to contents of flask, on this being heated the alcohol passes off, carrying the water with it, leaving the dry resins and fatty acids. These are dissolved in 10 volumes of absolute alcohol, any residue is added to the resins obtained below, from carrying out this process. Dry HCl acid gas is passed into this solution, and cooled by ice until saturated. Hot water is run into flask and its contents boiled over a free flame, taking care at incipient ebullition to prevent frothing.

The contents of flask are cooled and shaken out with ether, which dissolves the resins and resin acids; dilute alcoholic potash (2·5 grammes potassium hydroxide, 200 c.c. water, 20 c.c. alcohol) is added to the ether solution and shaking continued. This dissolves the resin acids which, together with any resins, are drawn off, leaving esters of linseed oil acids in ethereal layer. The resin soap solution is acidified, the acids dissolved in ether, the residue insoluble in alcohol, mentioned above, added to solution and whole evaporated in small beaker on water-bath. A small quantity of absolute alcohol is added and evaporation repeated. This removes any water; portions of material in beaker are chipped out, dried over sulphuric acid, and iodine and bromine numbers determined. From results by different observers it was thought that Hubl's iodine value could be used as a means of discrimination between a pure varnish resin and one adulterated with rosin. The iodine figures by Schmidt and Erban are as follows: Rosin 11·7, Angola copal, melted 42. Williams gives rosin 112, copal 130 to 138. The iodine number was determined as usual, using Hubl's method by solution in chloroform, and, except with samples A and B, the iodine was allowed to act for four hours; in these cases it acted for twenty-four. *N.B. Recovered*

resins cannot be kept much longer than one month without hardening to such an extent as to be insoluble in chloroform and carbon tetrachloride.

TABLE CLXXXII.—IODINE NUMBERS OF RESINS OBTAINED FROM VARIOUS VARNISHES.

Sample	Composition.	Maker.	Iodine Nos.	
A	Quick-rubbing varnish—pure kauri	B. Co.	64·1	68·2
B	" " "	"	68·6	59·3
C	Elastic " " "	"	46·4	47·1
D	" " " "	"	48·9	47·5
E	Pure rosin varnish	G. Co.	68·2	69·4
F	" "	"	64·4	64·3
G	Half rosin and half kauri varnish	"	67·5	69·3
H	One-fourth rosin and three-fourths kauri varnish .	"	62·2	62·5

Samples A and B, C and D, E and F were the same varnishes, but worked through separately. By comparing E, pure rosin, with G, half rosin and half kauri, practically no difference is seen in iodine numbers, hence these cannot be used to judge the purity of a varnish. It was therefore hoped that McIlhiney's bromine absorption method process would give results of more value. The method as given by him (this treatise, Vol. I, pp. 121-2) was applied to the resins extracted as detailed above with the results in Table II. The last eight results were obtained by a different operator carrying through the method at two different times. The results do not agree very well, although certain results, particularly the pure rosin E, and the one-fourth rosin varnishes H, are as close as can be expected. The difficulty seems due to emulsification of carbon tetrachloride with potassium iodide, which masks the end-point. Tendency to emulsification seems less with a pure rosin than with a kauri varnish.

TABLE CLXXXIII.—BROMINE NUMBERS OF VARIOUS RESINS OBTAINED FROM VARNISHES (GILL).

Sample	Composition.	Addition.	Substitution.	Total.
A	Pure kauri	54·3	26·3	106·9
A	"	60·5	26·0	112·4
B	"	57·5	23·6	104·7
C	"	75·5	3·3	82·1
C	"	76·6	4·7	86·0
E	Pure rosin	10·9	45·2	101·4
E	"	9·9	44·7	99·9
G	Half rosin and half kauri	21·2	54·2	129·6
"	" "	12·2	47·9	108·1
H	One-fourth rosin and three-fourths kauri .	44·9	36·5	111·9
"	" " "	50·9	35·8	122·0
E	Pure rosin	5·9	45·4	96·7
		0·4	50·1	100·6
		6·0	54·2	114·4
		1·1	58·1	117·3
H	One-fourth rosin and three-fourths kauri .	45·2	34·4	114·0
		51·0	31·5	114·0
		37·2	35·1	107·4
		42·0	33·5	109·0

It is, however, easy to determine from substitution values in table which varnishes contain rosin, evidently E, G, and H. There is so much irregularity in the numbers that the method would not seem a satisfactory quantitative one. The method was modified as follows: Such quantities of resin were employed that if 20 c.c. of N/3 bromine solution were used, the amount of bromine left after a certain time was very nearly equal to amount which had acted upon the resin. Time of action of bromine was three minutes. From 0·4 to 0·5 gramme of resin was weighed into a 50 c.c. graduated flask, dissolved in carbon tetrachloride and brought to mark with same; 10 c.c. were used for each determination. Window glass and black rosin were used to familiarize operator with method; in some cases an insoluble residue remained after treatment with the solvent—the clear liquid only was employed. It was found, however, that there was no difference as to whether this or the turbid liquor were used. Table III. shows a comparison of McIlhiney's original method and this modification: window-glass rosin was used.

TABLE CLXXXIV.—BROMINE NUMBERS OF ROSIN BY VARIOUS METHODS (GILL).

Total.	Added	Substituted	
125·5	23·3	51·1	original.
119·3	14·6	52·3	
102·8	24·4	39·2	clear solution.
103·0	23·8	39·6	
102·3	22·7	39·8	modified turbid solution.
101·8	25·5	38·1	

The method as modified was applied to resins from varnishes B, F, and H from Table II., and also to a suspected varnish I.

TABLE CLXXXV.—BROMINE NUMBERS OF VARIOUS RESINS (GILL).

Sample.	Composition	Total.		Bromine Added		Substituted	
B	Pure kauri . . .	108·7	107·7	70·1	73·8	19·3	17·0
F	,, rosin . . .	80·4	84·4	1·6	3·1	39·4	40·6
H	¼ rosin ¾ kauri . .	91·4	84·4	34·5	28·6	28·5	22·9
I	Unknown . . .	76·4	76·4	45·3	41·9	15·5	17·3

Sample I. is evidently not adulterated with rosin, as was shown by other tests. The results from the Hubl and the McIlhiney processes being so unsatisfactory from a quantitative point of view, the saponification, free acid, and ester values of these various resins were determined. These were determined in the usual way, as described in Gill's "Handbook of Oil Analysis" (the ester value is of course the difference between the two).

TABLE CLXXXVI.—SAPONIFICATION, FREE ACID, AND ESTER VALUES OF RESINS FROM VARIOUS VARNISHES (GILL).

Sample.	Composition.	Maker.	Saponification.	Free Acid.	Ester.	Average.
E	Pure rosin, No. 1	G. Co.	182·3	160·1	22·2	23·1
	" " " 6	"	185·7	161·7	24·0	
	Ordinary rosin not run	"	172·3	159·7	12·6	
H	One-fourth rosin, three-fourths kauri, No. 5	"	134·8	62·0	72·8	75·3
	One-fourth rosin, three-fourths kauri, No. 7	"	121·6	43·9	77·7	
G	Half rosin and half kauri, No. 3	"	143·5	88·0	55·5	55·5
	Kauri gum		124·2	41·0	83·2	84·0
	" No. 2		129·7	45·0	84·7	

Using average ester values obtained and usual formula $x = \frac{100(I - n)}{m - n}$ for calculating percentage of adulteration, the three-quarters kauri varnish figures 85 per cent, and the half and half kauri and rosin 53 per cent. It would seem that this method is fairly satisfactory, but requires confirmation by other observers before implicit trust can be placed in it.

Variations in the Viscosity of Alcoholic Solutions of Different Resins and Mixtures of Resins but of equal Resin Content by weight per gallon.—The effect of adding rosin to a shellac spirit varnish is seen in the following results by Davidson :—

"P B Pure" Button lac, 3 lb. per gall. alcohol had viscosity (Redwood's) at 70° F. of					88 secs.
Amer. E. rosin	"	"	"	"	40 "
Mixture containing 10 per cent rosin	"	"	"	"	70 "
Mixture containing 20 per cent rosin	"	"	"	"	64 "

But experimental results of this nature should be complete. The calculated viscosity of the 10 per cent mixture is 83·2 and of the 20 per cent mixture is 78·4. It will be seen at once by a glance at Table CLXXI. in how far the absence of the density of these varnishes detracts from any intrinsic value of such data. There is room for much good work being done in this direction, more especially in such technical schools like the Borough Polytechnic, where oil and colour trade research work is conducted under the guidance and instruction of those actively engaged in the industry.

TABLE CLXXXVII.—COMPARATIVE VISCOSITY OF ALCOHOL AND WATER.

Temp.	Water.		Alcohol	
	η	Z	η	Z.
0° C.	0·018086	1	0·01846	1·01
5	0·015301	0·84	0·01637	0·91
10	0·013257	0·73	0·01493	0·82
15	0·011503	0·63	0·01345	0·75
20	0·010164	0·56	0·01252	0·68
30	0·008121	0·44	0·01027	0·56
40	0·006638	0·36	0·00856	0·47
50	0·005697	0·31	0·00718	0·39
60	0·004865	0·26	0·00616	0·33

η = C.G.S. units. Z = specific viscosity, water at 0° C. as unity.

TABLE CLXXXVIII.—SPECIFIC VISCOSITY OF CERTAIN VOLATILE SOLVENTS.

Solvent	Z at 15° C.	Z at 20° C.	Solvent	Z at 15° C.	Z at 20° C.
Acetone . .	0·23	0·22	Isobutyl alcohol .	2·75	2·33
Ether . .	0·14	0·13	Acetic acid .	0·76	0·70
Aldehyde . .	0·21	0·21	Methyl alcohol .	0·37	0·35
Allyl alcohol .	1·04	0·92	Nitrobenzene . .	1·24	1·14
Amyl alcohol .	3·09	2·64	Toluene . . .	0·35	0·33
Benzene . .	0·39	0·36	m-Xylene . .	0·39	0·37
Butyl alcohol .	2·08	1·82			

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